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PRECIPITATION OF PALLADIUM WITH DIMETHYLGLYOXIME IN THE PRESENCE OF FERRIC SALTS

Yu. V. Morachevskii, I. A. Tserkovnitskaya and Z. G. Golubtsova

Leningrad State University

One of the most convenient and widely used methods for the quantitative determination of palladium is its precipitation from acid solutions with dimethylglyoxime with subsequent weighing of the palladium dimethylglyoxime, dried at 110°.

Previously, one of us [1] noted that if ferric salts were present in the solution analyzed, then the precipitation of palladium with dimethylglyoxime was incomplete and under certain conditions, no precipitate at all formed. We then showed that in the precipitation of palladium with dimethylglyoxime from solutions containing Cr^{3+}, Al^{3+} and Fe^{2+}, similar phenomena were not observed.

We found no direct indications in the literature on the role of iron in the precipitation of palladium with dimethylglyoxime. However, Bobtelsky and Mayer [2] emphasized that in the microdetermination of palladium with dimethylglyoxime in the presence of iron, it was necessary to use masking reagents.

We investigated the effect of iron on the precipitation of palladium from hydrochloric, sulfuric, nitric and perchloric acid solutions of various concentrations. Preliminary experiments showed the limits of acid concentration within which the completeness of palladium separation was not reduced.

As experiments showed, precipitation of palladium with dimethylglyoxime was still practically complete in 1.5 N solutions of perchloric, nitric and hydrochloric acids; in sulfuric acid solution, palladium was one hundred percent precipitated from 2 N solution also. The effect of raising the acidity of the solution on the completeness of palladium precipitation was expressed most strongly in perchloric acid solutions and least of all in sulfuric acid. While palladium was not precipitated by dimethylglyoxime from 3 N perchloric acid solution, 99% of the palladium was precipitated from sulfuric acid solutions of the same concentrations.

EXPERIMENTAL

1. Precipitation of palladium with dimethylglyoxime in the presence of $FeCl_3$ in a hydrochloric acid medium. In the experiments presented in Table 1, the iron content and acidity of the solution was varied with a constant palladium concentration in the original solution (50 ml). With an increase in the iron concentration of a solution, the precipitation of palladium by dimethylglyoxime became less and less complete. At low concentrations of hydrochloric acid in the solution, the effect of iron on the percentage separation of palladium was greater than in more acid solutions. Thus, in 0.1 N hydrochloric acid solution, the complete absence of precipitation of palladium by dimethylglyoxime begins even at a 50-fold (gram-atoms) excess of iron over palladium. In 1 N solution with the same ratio of palladium and iron, 87% of the palladium is precipitated.

2. Precipitation of palladium with dimethylglyoxime in the presence of $Fe_2(SO_4)_3$ in a sulfuric acid medium. The results of the experiments are presented in Table 2.

The experiments showed that here the presence of iron had a greater effect on the completeness of palladium precipitation in solutions of lower acidity than at higher acid concentrations. However, in sulfuric acid solutions, with an increase in iron concentration there was a more gradual decrease in the percent precipitation

TABLE 1

Expt. No.	Pd : Fe (g-at.)	Grams taken		Conc. of HCl in solution (N)	Palladium found in precipitate	
		palladium	iron		g	%
1	1 : 2	0.0047	0.0048	0.1	0.0047	100
2	1 : 10		0.0240		0.0045	96
3	1 : 50		0.1152		0.0000	0
4	1 : 2	0.0047	0.0048	0.5	0.0047	100
5	1 : 10		0.0240		0.0046	98
6	1 : 50		0.1152		0.0007	15
7	1 : 100		0.2400		0.0000	0
8	1 : 2	0.0047	0.0048	1.0	0.0047	100
9	1 : 10		0.0240		0.0047	100
10	1 : 50		0.1152		0.0041	87
11	1 : 100		0.2400		0.0013	28
12	1 : 200	0.0050	0.5000		0.0002	4
13	1 : 400	0.0047	0.9000		0.0000	0
14	1 : 2	0.0050	0.0050	1.5	0.0050	100
15	1 : 10		0.0250		0.0050	100
16	1 : 50		0.1250		0.0043	86
17	1 : 100		0.2500		0.0036	72
18	1 : 200		0.5000		0.0007	14

TABLE 2

0.0047 g of Palladium was Taken in All Experiments

Expt. No.	Pd : Fe (g-at.)	Iron taken (in g)	Conc. of H_2SO_4 in solution (N)	Palladium found in precipitate	
				g	%
1	1 : 2	0.0047	0.1	0.0045	96
2	1 : 10	0.0235		0.0042	89
3	1 : 50	0.1175		0.0000	0
4	1 : 2	0.0047	0.5	0.0047	100
5	1 : 10	0.0235		0.0047	100
6	1 : 50	0.1175		0.0042	89
7	1 : 100	0.2350		0.0000	0
8	1 : 2	0.0047	1.0	0.0047	100
9	1 : 10	0.0235		0.0047	100
10	1 : 50	0.1175		0.0042	89
11	1 : 100	0.2350		0.0038	81
12	1 : 200	0.4700		0.0003	6
13	1 : 400	0.9400		0.0000	0
14	1 : 2	0.0047	2.0	0.0044	94
15	1 : 10	0.0235		0.0044	94
16	1 : 50	0.1175		0.0044	94
17	1 : 100	0.2350		0.0044	94
18	1 : 200	0.4700		0.0008	17
19	1 : 400	0.9400		0.0000	0

TABLE 3

0.0050 g of Palladium was Taken in All Experiments

Expt. No.	Pd : Fe (g-at.)	Iron taken (in g)	Conc. of HNO_3 in solution (N)	Palladium found in precipitate	
				g	%
1	1 : 1	0.0026	0.1	0.0044	88
2	1 : 2	0.0052		0.0043	86
3	1 : 4	0.0105		0.0035	70
4	1 : 10	0.0262		0.0010	20
5	1 : 20	0.0524		0.0000	0
6	1 : 1	0.0026	0.5	0.0047	94
7	1 : 2	0.0052		0.0047	94
8	1 : 4	0.0105		0.0047	94
9	1 : 10	0.0262		0.0041	82
10	1 : 20	0.0524		0.0028	56
11	1 : 1	0.0026	1.0	0.0050	100
12	1 : 2	0.0052		0.0050	100
13	1 : 4	0.0105		0.0048	96
14	1 : 10	0.0262		0.0047	94
15	1 : 20	0.0524		0.0033	66

TABLE 4

0.0050 g of Palladium was Taken in All Experiments

Expt. No.	Pd : Fe (g-at)	Iron taken (in g)	Conc. of $HClO_4$ (N)	Palladium found in precipitate	
				g	%
1	1 : 1	0.0024	0.1	0.0049	98
2	1 : 4	0.0094		0.0047	94
3	1 : 10	0.0235		0.0033	70
4	1 : 20	0.0470		0.0000	0
5	1 : 1	0.0024	0.5	0.0049	98
6	1 : 4	0.0094		0.0048	96
7	1 : 10	0.0235		0.0044	88
8	1 : 20	0.0470		0.0024	48
9	1 : 1	0.0024	1.0	0.0049	98
10	1 : 4	0.0094		0.0046	92
11	1 : 10	0.0235		0.0041	82
12	1 : 20	0.0470		0.0032	64
13	1 : 1	0.0024	1.5	0.0046	92
14	1 : 4	0.0094		0.0045	90
15	1 : 10	0.0235		0.0038	70
16	1 : 20	0.0470		0.0022	44

of palladium. While in 0.5 N hydrochloric acid solution, at a Pd : Fe gram-atom ratio of 1 : 50, only 15% of the palladium was precipitated, in a sulfuric acid solution of the same concentration and with the same concentration of iron, 89% of the palladium was precipitated.

3. Precipitation of palladium with dimethylglyoxime in the presence of $Fe(NO_3)_3$ in a nitric acid medium. The results of the experiments are presented in Table 3. The effect of iron on the completeness of palladium precipitation appeared here even more sharply than in hydrochloric acid solutions. Even a 20-fold excess of iron over palladium in 0.1 N nitric acid solution prevented complete precipitation of palladium, while under the same conditions in hydrochloric acid solution, 70% of the palladium was precipitated. In 1 N nitric acid solution, at a Pd : Fe gram-atom ratio of 1 : 20, only 66% of the palladium was precipitated, while in hydrochloric acid, even at a Pd : Fe ratio of 1 : 50, 87% of the palladium was precipitated.

4. Precipitation of palladium with dimethylglyoxime in the presence of ferric iron in a perchloric acid medium. The results obtained are presented in Table 4.

The dependence of the completeness of palladium precipitation on the amount of iron present in the solution in this case was also connected with the concentration of acid in the solution. In 0.1 N perchloric acid solution, the complete absence of precipitation of palladium by dimethylglyoxime began even at a Pd : Fe ratio of 1 : 20 and in 1 N solution with the same amount of iron, 64% of the palladium was still precipitated. In a perchloric acid medium, the effect of iron on the precipitation of palladium was similar to or slightly less than in nitric acid solutions, but considerably more than in hydrochloric and sulfuric acid solutions. While in 0.5 N perchloric acid solution, with a 10-fold excess of iron over palladium, 88% of the palladium was precipitated, in nitric acid solution of the same concentration, 82%, in hydrochloric acid solution, 98%, and in sulfuric acid solution, 100% of the palladium was precipitated.

The results obtained indicate that in acid solutions, dimethylglyoxime, ferric iron, and palladium react together to form a complex compound, whose nature we have not yet established.

At the present time we are making a spectrophotometric investigation of the palladium -- iron -- dimethylglyoxime system.

SUMMARY

1. A study was made of the effect of solution acidity on the precipitation of palladium by dimethylglyoxime. It was established that palladium was precipitated completely from 1.5 N solutions of perchloric, nitric and hydrochloric acid solutions and from 2 N sulfuric acid solutions; a further increase in the acid concentration led to a fall in the percent of palladium precipitated.

2. A study was made of the effect of ferric iron on the precipitation of palladium by dimethylglyoxime in hydrochloric, sulfuric, nitric and perchloric acid solutions.

It was established that the presence of Fe^{3+} in the solution led to incomplete precipitation of palladium. The effect of iron was maximal in perchloric and nitric acid solutions; it was greater, the lower the acidity of the solution.

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SELECTIVITY OF ACTION OF NICKEL DEPOSITED ON ALUMINUM OXIDE CATALYSTS

N. V. Berunova, A. A. Balandin and L. Kh. Freidlin

Institute of Organic Chemistry, Academy of Sciences USSR

It was previously established that the reduction of a mixture of nickelous oxide and aluminum oxide, prepared by coprecipitation and treatment with water vapor under pressure, gave a nickel-aluminum oxide catalyst, in whose presence C=C and C=O double bonds were reduced, while an aromatic bond was not hydrogenated [1]. In the present work a study was made of the selectivity of action of similar catalysts prepared from nickelous oxide deposited on aluminum oxide and treated with water vapor or carbon dioxide.

EXPERIMENTAL

Preparation of catalysts. Experimental conditions. The aluminum oxide used had a specific surface of 280 m^2/g (calculated according to BET from data on benzene adsorption). The pore radii lay within the limits of 20 – 120 A° and the maximal pore volume occurred at a radius of 40 A.

The aluminum oxide was impregnated with a 0.5 M aqueous solution of nickel nitrate, which was then evaporated slowly and the mixture fired for 4 hours at 400°. Its composition was 12.5% nickelous oxide and 87.5% aluminum oxide.

The mixture of nickelous oxide and aluminum oxide prepared was placed in a quartz beaker, which was inserted into a rotating, stainless steel autoclave. The autoclave was first heated to 350° and water introduced by means of a special dosing apparatus. This made it possible to consider the duration of the treatment at the given temperature. After the addition of the water, the temperature in the autoclave came up to the given value again after 10 – 15 minutes. The mixture was treated at 350° for 2 hours. After the heating, the steam was expelled from the autoclave. In treatment with carbon dioxide,* the mixture of oxides was placed directly into the autoclave, into which carbon dioxide was introduced from a tank.

The treated samples were fired in a stream of dry air at 400° for 4 hours, formed into cylinders, 6 × 4 mm in size and reduced with electrolytic hydrogen at 350°. To remove oxygen, the hydrogen was passed through a bottle with pyrogallol and then at 300° through a tube filled with reduced copper. The hydrogen was freed from moisture and other impurities by passage through a column with silica gel and bottles with calcium chloride and phosphorus pentoxide.

The activity of the catalyst was tested in the hydrogenation of benzene, octene-3 or styrene and also in the dehydrogenation of cyclohexane in a stream of hydrogen by the usual procedure, namely in a flow system or in an autoclave. Benzene was hydrogenated at atmospheric pressure at 120 or 180° and in an autoclave at a pressure of 120 atm at 170°. Mixtures of octene - 3 with benzene and with styrene also were hydrogenated at atmospheric pressure at 130, 180 and 160°, respectively. Cyclohexane was dehydrogenated at 300°. The volume rate in all experiments was 0.3 $hour^{-1}$. The degree of conversion of benzene and cyclohexane was determined refractometrically [2] and the degree of hydrogenation of octene-3 and the ethylene bond of styrene by bromination [3]. The experiments are presented in the tables in the order in which they were performed.

* According to specifications, the carbon dioxide contained not less than 98% of carbon dioxide and up to 2% of oxygen and nitrogen; no other impurities were present.

TABLE 1

Water vapor pressure (in atm.)	Duration of reduction at 350° (in hour)	Substance hydrogenated	Hydrogenation temperature	Degree of hydrogenation (in %)	Degree of dehydrogenation of cyclohexane at 300° (%)
10—20	10	Benzene	120°	83.0	21.6
	25	Benzene	120	92.0	33.7
35	10	Benzene	120	0.4	—
		Benzene	180	0.6	—
	20	Benzene	120	0.4	
		Benzene	180	2.3	4.0
60	10	Benzene	120	0.4	—
		Benzene	180	1.2	—
	20	Benzene	180	1.2	3.6
90—100	10	Benzene	120	0.1	9.0
		Octene-3	130	100.0	—
	20	Benzene	120	1.0	—
	30*	Benzene	120	0.4	—
		Benzene	180	0.1	
		Mixture benzene (90%) octene-3 (10%)	180	— 100.0	— —
		Styrene	160	97.5**	—
		Benzene***	170	0.2	—
90—100****	10	Benzene	120	0.0	6.0
		Benzene	180	1.2	
		Octene-3	130	97.9	—
	25	Benzene	120	0.3	
		Benzene	180	1.2	—

* The last 10 hours at 400°.

** The degree of hydrogenation of the ethylene bond is given.

*** At a pressure of 120 atm.

**** The aluminum oxide was used as lumps, while in the rest of the experiments the aluminum oxide was first ground to a powder.

Selectivity of action of catalysts prepared by reduction of a mixture of nickelous oxide and aluminum oxide, treated with water vapor. Tests were first made on a catalyst prepared by reduction of a mixture of nickelous oxide and aluminum oxide, which had not been preliminarily treated with water vapor. The catalyst had a high activity: the degree of hydrogenation of benzene at 180° was 99.8% and the degree of dehydrogenation of cyclohexane, 92.0%.

The data in Table 1 show that the catalyst obtained from a mixture of nickelous oxide and aluminum oxide, treated with water vapor at a pressure of 10 — 20 atm. and reduced at 350° for 25 hours, produced a high degree of hydrogenation of benzene, namely 92.0%, while the degree of dehydrogenation of cyclohexane over it was only 33.7%. Catalysts prepared from a mixture of oxides treated with water vapor at a pressure of 35 — 60 atm were inactive in the hydrogenation of benzene and showed low activity in the dehydrogenation of cyclohexane. A catalyst prepared from a mixture of nickelous oxide and aluminum oxide, treated with water vapor at a pressure of 90 — 100 atm did not produce hydrogenation of benzene, regardless of the duration of reduction with hydrogen, even at a pressure of 120 atm.

Hydrogenation of styrene yielded a catalyzate with n_D^{20} 1.4959. Determination of the bromine number showed that the ethylene bond in styrene was 97.5% hydrogenated. From a consideration of the refractive index value and the bromine number it follows that the ethylene bond was hydrogenated selectively over this catalyst, while the benzene nucleus remained untouched.

TABLE 2

Processing conditions with carbon dioxide			Duration of reduction at 350° (in hours)	Hydrogenation temperature	Degree of hydrogenation (in %)	Degree of dehydrogenation of cyclohexane at 300° (%)	Degree of hydrogenation of octene-3 at 130° (%)
temperature	pressure (in atm.)	duration (in hrs.)					
300°	150	2	10	120°	96.0	—	—
350	150	2	10	120	12.0	51.8	—
				180	85.6		
400	150	2	10	120	0.0	7.7	—
				180	0.0		
			20	120	0.0	10.6	100.0
				180	0.0		
			30	120	0.0	—	—
				180	0.0	—	—
350	100	2	10	120	78.4	61.2	—
350	200	2	10	120	1.2	36.8	—
				180	58.0		
			20	120	7.6	52.0	100.0
				180	95.0		
350	200	10	10	120	0.0	12.0	—
				180	3.2		
			20	120	0.4	28.4	—
				180	6.0		
			30	120	4.6	33.2	100.0
				180	15.0		
			40*	120	12.0	61.0	—
				180	87.4		

* The last 10 hours at 400°.

In the experiments described here and in the previous work [1], a study was made of the activity of catalysts in the hydrogenation of one individual substance. It was interesting to determine how the hydrogenation of a mixture proceeded. As the data in Table 1 show, in a mixture of 90% benzene and 10% octene-3, the latter was hydrogenated completely at 180° and atmospheric pressure.

Selectivity of action of catalysts prepared by reduction of a mixture of nickelous oxide and aluminum oxide, treated with carbon dioxide. Table 2 shows the results of experiments with catalysts prepared by reduction of a mixture of nickelous oxide and aluminum oxide, prepared by deposition and treatment with carbon dioxide. From the data in the table it follows that with an increase in the temperature and pressure and also with an increase in the duration of treatment with carbon dioxide, the selectivity of action of the catalyst increasd. Thus, with the temperature of treatment with carbon dioxide raised from 300 to 400°, the activity of the catalyst in the hydrogenation of benzene and dehydrogenation of cyclohexane decreased sharply. In the presence of a catalyst, prepared by a 20 hour reduction of nickelous oxide and aluminum oxide, treated with carbon dioxide at 400°, the degree of dehydrogenation of cyclohexane was 10.6%. At 180°, benzene was not hydrogenated al all, while octene-3 was 100.0% hydrogenated over this catalyst.

When the carbon dioxide pressure was raised from 100 to 200 atm., the degree of hydrogenation of benzene at 120° fell sharply. The duration of treatment also had a great effect on the activity of the catalyst. With a 2 hour treatment with carbon dioxide, after even 20 hours reduction with hydrogen, the degree of hydrogenation of benzene at 180° reached 95.0%, while the degree of dehydrogenation with cyclohexane was 52.0%. With a 10 hour treatment with carbon dioxide under the same conditions and reduction for 20 hours, the degree of hydrogenation of benzene was only 0.4% and the degree of dehydrogenation of cyclohexane was 28.4%. However, after reduction with hydrogen for 40 hours (the last 10 hours at 400°), the degree of hydrogenation of benzene reached 87.4% and the degree of dehydrogenationof cyclohexane was 61.6%. Thus, poisoning with carbon dioxide has a reversible character. Octene-3 was hydrogenated completely on all samples.

The results presented show that treatment of nickelous oxide and aluminum oxide with carbon dioxide may be used to regulate the activity of a nickel deposited on aluminum oxide catalyst and achieve specificity in its action.

SUMMARY

1. An investigation was made of the effect of treating a mixture of nickelous oxide and aluminum oxide with water vapor and carbon dioxide under pressure on the activity of catalysts prepared from it.

2. It was established that deposited catalysts, prepared by treatment with water vapor, selectively hydrogenated the ethylene bond of octene-3 or styrene in the presence of an aromatic bond.

3. It was shown that treatment of a mixture of nickelous oxide and aluminum oxide with carbon dioxide under pressure could be used to regulate the activity of catalysts prepared from it and confer specificity of action on them.

4. It was established that the deactivation of a catalyst by treatment with carbon dioxide, in contrast to treatment with water vapor, had a reversible character.

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THERMODYNAMIC CHARACTERISTICSOF CALCIUM, GALLIUM, INDIUM AND THALLIUM COMPOUNDS

P. G. Maslov

Military Mechanical Institute

In accordance with methods developed in previous papers [1 — 4], the value of a thermodynamic property A of any mixed halides of the type $BF_iCl_jBr_kI_q$ in solution or liquid or solid states may be found simply and accurately by a formula of the form:

$$A_{BF_iCl_jBr_kI_q} = \frac{1}{n}\left(iA_{BF_n} + jA_{BCl_n} + kA_{BBr_n} + qA_{BI_n}\right), \tag{1}$$

if the values of this property under the same conditions are known for the simplest representatives BF_n, BCl_n, BBR_n and BI_n of the same family of compounds. In relation (1) n = i + j + k + q, B and B is a group of atoms in the molecule, which remains unchanged during replacements of the various halogens.

Similarly, if there are the general formulas

$$A_{BF_n \cdot mR} = a_{BF_n \cdot mR} + a_2 \cdot m, \tag{2}$$

$$A_{BCl_n \cdot mR} = a_{BCl_n \cdot mR} + a_2 \cdot m, \tag{3}$$

$$A_{BBr_n \cdot mR} = a_{BBr_n \cdot mR} + a_2 \cdot m, \tag{4}$$

$$A_{FI_n \cdot mR} = a_{BI_n \cdot mR} + a_2 \cdot m \tag{5}$$

for determining the thermodynamic property A of families of the simplest compounds $BF_n \cdot mR$, $BCl_n \cdot mR$, $BBR_n \cdot mR$ and $BI_n \cdot mR$ (m = 0,1,2,3. . .), from the expression (1) it is easy to find general formulas for calculating the property A of families of more complex halides of the type $BF_iClBr_kI_q \cdot mR$; here

$$A_{BF_iCl_jBr_kI_q \cdot mR} = \frac{1}{n}\left(iA_{BF_n \cdot mR} + jA_{BCl_n \cdot mR} + kA_{BBr_n \cdot mR} + qA_{BI_n \cdot mR}\right), \tag{6}$$

or, taking into account formulas (2) - (5),

$$A_{BF_iCl_jBr_kI_q \cdot mR} = \frac{1}{n}\left(iA_{BF_n \cdot mR} + jA_{BCl_n \cdot mR} + kA_{BBr_n \cdot mR} + qA_{BI_n \cdot mR}\right) + a_2 \cdot m. \tag{7}$$

In formulas (6) and (7), as above, n = i + j + k + q; R is a group repeated in each of the molecules, for example, in crystal hydrates R = H_2O and in ammoniates R= NH_3 and m is any number, both integral and fractional.

By the methods indicated above [1 - 4], in the present work general approximate formulas were obtained for determining the heats of formation ($-\Delta H_f^\circ$), the free energies ($-\Delta Z_f^\circ$), the logarithms of the equilibrium constants ($\lg K_f$), the entropies and the molecular heat capacities (C_p°) at 25° C for families of gallium, indium and thallium compounds, mainly in the crystalline phase and partly in solution. Data from papers [5 — 11] were taken

TABLE 1

General Formulas for Determining the Thermodynamic Properties of Gallium, Indium and Thallium Compounds in the Crystalline State at 25° C

Compound	$-\Delta H_f^0$ (in kcal/ mole)	Value of m	Compound	$-\Delta H_f^0$ (in kcal/mole)	Value of m, n
$GaCl_3 \cdot mNH_3$	$193.7 + 19m$	$m \geq 3$	$InClBr_2 \cdot mNH_3$	$165 + 19m$	$m \geq 4$
$GaBr_3 \cdot mNH_3$	$167.7 + 19m$	$m \geq 4$	$InClI_2 \cdot mNH_3$	$140 + 19m$	$m \geq 4$
$GaI_3 \cdot mNH_3$	$126 + 19m$	$m \geq 4$	$InBrI_2 \cdot mNH_3$	$131 + 19m$	$m \geq 4$
$GaCl_2Br \cdot mNH_3$	$185 + 19m$	$m \geq 4$	$InClBrI \cdot mNH_3$	$152 + 19m$	$m \geq 4$
$GaCl_2I \cdot mNH_3$	$165 + 19m$	$m \geq 4$	$TlCl_3 \cdot nH_2O$	$83.7 + 71n$	$n \geq 0$
$GaBr_2I \cdot mNH_3$	$153.8 + 19m$	$m \geq 4$	$TlBr_3 \cdot nH_2O$	$50.6 + 71n$	$n \geq 0$
$GaClBr_2 \cdot mNH_3$	$176.3 + 19m$	$m \geq 4$	$TlCl_2Br \cdot nH_2O$	$72.7 + 71n$	$n \geq 0$
$GaClI_2 \cdot mNH_3$	$148.6 + 19m$	$m \geq 4$	$TlClBr_2 \cdot nH_2O$	$61.6 + 71n$	$n \geq 0$
$GaBrI_2 \cdot NH_3$	$139.9 + 19m$	$m \geq 4$	$TlBrO_3 \cdot nH_2O$	$24 + 71n$	$n \geq 0$
$GaClBrI \cdot mNH_3$	$162.5 + 19m$	$m \geq 4$	$Tl_2SO_4 \cdot nH_2O$	$221.7 + 71n$	$n \geq 0$
$InCl_3 \cdot mNH_3$	$182.9 + 19m$	$m \geq 4$	$TlCl \cdot mNH_3$	$46 + 19m$	$m \geq 2$
$InBr_3 \cdot mNH_3$	$156.4 + 19m$	$m \geq 4$	$TlCl_3 \cdot mNH_3$	$88 + 19m$	$m \geq 2$
$InI_3 \cdot mNH_3$	$118 + 19m$	$m \geq 4$	$TlBr \cdot mNH_3$	$39 + 19m$	$m \geq 2$
$InCl_2Br \cdot mNH_3$	$174.1 + 19m$	$m \geq 4$	$TlI \cdot mNH_3$	$27 + 19m$	$m \geq 2$
$InCl_2I \cdot mNH_3$	$161.3 + 19m$	$m \geq 4$			
$InBr_2I \cdot mNH_3$	$144 + 19m$	$m \geq 4$			

Compound	$-\Delta H_f^0$ (kcal/ mole)	$-\Delta Z_f^0$ (kcal/ mole)	$\log K_f$	S^0 (in cal/ / mole · deg)	value of n
$TlIO_3 \cdot nH_2O$		$47.6 + 56.89n$	$34.89 + 41.702n$		$n \geq 0$
$TlNO_3 \cdot nH_2O$*	$58 + 71n$	$36.07 + 56.89n$	$26.44 + 41.702n$	$38.2 + 9.866n$	$n \geq 0$

* Formula written for crystals of modification III.

TABLE 2

Comparison of Heats of Formation ($-\Delta H_f^\circ$) of Ga, In and Tl compounds at 25° C, Calculated by the Formulas in Table 1, With Available Experimental Values [1 – 5]

Compound	Calculated $-\Delta H_f^\circ$ (in kcal/mole)		Compound	$-\Delta H_f^0$ (in kcal/mole) for crystals		Compound	$-\Delta H_f^0$ (in kcal/mole) for crystals	
	crystals	solution		calculated	experiment		calculated	experiment
$GaCl_3$	(125.4)*	(170.5)*	$InCl_3 \cdot NH_3$	—	(163.1)*	$GaI_3 \cdot 9NH_3$	297	(298.7)
$GaBr_3$	(92.4)*	(130.8)*	$InI_3 \cdot NH_3$	—	(87.6)*	$GaI_3 \cdot 13NH_3$	373	(374.8)
GaI_3	(51.2)*	(84.2)*	$InCl_2I \cdot NH_3$	137.9	—	$InBr_3 \cdot 5NH_3$	251	(246.9)
$GaCl_2Br$	114.4	157.3	$InClI_2 \cdot NH_3$	112.8	—	$InBr_3 \cdot 7NH_3$	—	(289.4)*
$GaCl_2I$	100.7	141.7	$InCl_3 \cdot 2NH_3$	—	(195.5)*	$InBr_3 \cdot 5NH_3$	213	(201.9)
$GaBr_2I$	78.7	115.3	$InI_3 \cdot 2NH_3$	—	(117.7)*	$InI_3 \cdot 7NH_3$	—	(251)*
$GaClBr_2$	103.4	144.0	$InCl_2I \cdot 2NH_3$	169.6	—	$InI_3 \cdot 9NH_3$	289	(290.9)
$GaClI_2$	75.9	113.0	$InClI_2 \cdot 2NH_3$	143.6	—	$InI_3 \cdot 21NH_3$	517	(513.2)
$GaBrI_2$	64.9	99.7	$InCl_3 \cdot 3NH_3$	—	(227.9)*	$TlClBr_2 \cdot 4H_2O$	345.6	(346.3)
$GaClBrI$	89.7	128.5	$InBr_3 \cdot 3NH_3$	—	(193.3)*	$TlBrO_3$	—	(24.0)*
$InCl_3$	(128.4)*	(147.2)*	$InCl_2Br \cdot 3NH_3$	216.3	—	Tl_2SO_4	—	(221.7)*
$InBr_3$	(96.5)*	(113.9)*	$InClBr_2 \cdot 3NH_3$	204.8	—	$TlNO_3$ [1]	—	(58.01)*
InI_3	(55)*	(67.3)*	$InCl_3 \cdot 5NH_3$	277.9	(276.6)	$TlCl \cdot 2NH_3$	—	(103.4)*
$InCl_2Br$	117.8	136.1	$InCl_3 \cdot 15NH_3$	468	(465.4)	$TlCl_3 \cdot 3NH_3$	—	(145)*
$InCl_2I$	103.9	120.6	$GaCl_3 \cdot 5NH_3$	288.7	(285.6)	$TlBr \cdot 3NH_3$	—	(95.6)*
$InBr_2I$	82.7	98.4	$GaCl_3 \cdot 6NH_3$	308	(308)	$TlJ \cdot 3NH_3$	—	(84.1)*
$InClBr_2$	107.1	125	$GaCl_3 \cdot 8NH_3$	327	(328.5)	$[Tl(H_2O)_4]Cl_3$	—	[366.4]*
$InClI_2$	79.5	93.9	$GaBr_3 \cdot 5NH_3$	263	(256.1)	$[Tl(H_2O)_4]Br_3$	—	[333.9]*
$InBrI_2$	68.8	82.8	$GaBr_3 \cdot 6NH_3$	282	(280.4)	$[Tl(H_2O)_4]Cl_2Br$	355.6	—
$InClBrI$	93.3	109.5	$GaBr_3 \cdot 7NH_3$	301	(301.8)	$[Tl(H_2O)_4]ClBr_2$	344.7	[345.5]*
$TlCl_3$	(83.9)*	(92.3)*	$GaBr_3 \cdot 9NH_3$	339	(340.5)	$GaI_3 \cdot 20NH_3$	—	(516)*
$TlBr_3$	(50.6)*	(70.1)*	$GaI_3 \cdot 5NH_3$	221	(211.5)	$GaCl_3 \cdot 14NH_3$	—	(459.7)*
$TlCl_2Br$	72.8	59	$GaI_3 \cdot 6NH_3$	240	(237.7)	$GaBr_3 \cdot 14NH_3$	—	(433.7)*
$TlClBr_2$	61.7	81.2	$GaI_3 \cdot 7NH_3$	259	(259.6)	$GaBr_3 \cdot 4H_2O$	—	(334.6)*

* The data refer to crystals of modification III.

TABLE 3

General Formulas for Determining the Thermodynamic Properties of Calcium Compounds at 25° C

Compound	State	$-\Delta H_f^0$ (in kcal/mole) for crystal	n; m	Compound	State	$-\Delta H_f^0$ (in kcal/mole) for crystal	n; m; t
$CaO_2 \cdot nH_2O$	Crystalline	$152 + 71n$	$n \geq 0$	$t CaO \cdot mC_2H_5OH$	Crystalline	$166.8 + 69.05m$	$m > 0$
$CaCl_2 \cdot mCaO \cdot nH_2O$	»	$197 + 166.8m + 71n$	$m > 0$ $n \geq 0$	$CaCl_2 \cdot mC_2H_5OH$	»	$191.2 + 69.05m$	$m > 0$
$CaBr_2 \cdot mCaO \cdot nH_2O$	»	$174 + 166.8m + 71n$	$m > 0$ $n > 0$	$t CaO \cdot mCa(CN)_2 \cdot nH_2O$	»	$166.8t + 42.6m + 71n$	$t > 0$ $m \geq 0$ $n \geq 0$
$CaI_2 \cdot mCaO \cdot nH_2O$	»	$143 + 166.8m + 71n$	$m > 0$ $n > 0$	$Ca(NO_3)_2 \cdot mCH_3OH$	»	$219.2 + 61.88m$	$m \geq 0$
$CaClBr \cdot mCaO \cdot nH_2O$	»	$185 + 166.8m + 71n$	$m > 0$ $n > 0$	$CaI_2 \cdot 2RbI_2 \cdot nH_2O$	»	$216 + 71n$	$n \geq 0$
$CaClI \cdot mCaO \cdot nH_2O$	»	$170 + 166.8m + 71n$	$m > 0$ $n > 0$	$CaCl_2 \cdot 2Hg(CN)_2 \cdot nH_2O$	»	$75 + 71n$	$n \geq 0$
$CaBrI \cdot mCaO \cdot nH_2O$	»	$158 + 166.8m + 71n$	$m > 0$ $n > 0$	$CaCl_2 \cdot 2Hg(CN)_2 \cdot nH_2O$	Solution in 1000 H_2O	$77.5 + 71n$	$n \geq 0$
$CaN_2O_2 \cdot nH_2O$	»	$121.7 + 71n$	$n > 0$	$CaBr_2 \cdot 2Hg(CN)_2 \cdot nH_2O$	Crystalline	$56.1 + 71n$	$n \geq 0$
$CaCl_2 \cdot mNH_3$	»	$216 + 19m$	$m \geq 1$	$CaBr_2 \cdot 2Hg(CN)_2 \cdot nH_2O$	Solution in 1000 H_2O	$56 + 71n$	$n \geq 0$
$CaBr_2 \cdot mNH_3$	»	$197 + 19m$	$m > 1$	$CaI_2 \cdot 2Hg(CN)_2 \cdot nH_2O$	Crystalline	$32 + 71n$	$n \geq 0$
$CaI_2 \cdot mNH_3$	»	$164 + 19m$	$m \geq 2$	$CaI_2 \cdot 2Hg(CN)_2 \cdot nH_2O$	Solution in 1000 H_2O	$29.3 + 71n$	$n \geq 0$
$CaClBr \cdot mNH_3$	»	$206 + 19m$	$m \geq 2$	$CaClBr \cdot 2Hg(CN)_2 \cdot nH_2O$	Crystalline	$66 + 71n$	$n \geq 0$
$CaClI \cdot mNH_3$	»	$190 + 19m$	$m \geq 2$	$CaClI \cdot 2Hg(CN)_2 \cdot nH_2O$	»	$54 + 71n$	$n \geq 0$
$CaBrI \cdot mNH_3$	»	$181 + 19m$	$m \geq 2$	$CaBrI \cdot 2Hg(CN)_2 \cdot nH_2O$	»	$44 + 71n$	$n \geq 0$
$Ca(H_2PO_4)_2 \cdot mNH_3 \cdot nH_2O$	»	$751 + 71n + 19m$	$m \geq 0$ $n \geq 0$	$CaFe(CN)_6 \cdot nH_2O$	»	$105.6 + 71n$	$n \geq 0$
$CaHAsO_4 \cdot nH_2O$	Solution	$344 + 71n$	$n \geq 0$	$CaFe(CN)_6 \cdot nH_2O$	Solution in 1000 H_2O	$\sim (133 + 71n)$	$n \geq 0$

TABLE 3 (continued)

Compound	State	$-\Delta H_f^0$ (in kcal/ mole)	n; m	Compound	State	$-\Delta H_f^0$ (in kcal/ mole)	n; m; t
$Ca(H_2AsO_4)_2 \cdot nH_2O$	Solution	$\sim(561 + 71n)$	$n \geqslant 0$	$tCaO \cdot mAl_2O_3 \cdot nH_2O$	Crystalline	$166.8t + 373.6m + 71n$	$t > 0$ $m \geqslant 0$ $n \geqslant 0$
$Ca(C_2H_3O_2) \cdot nH_2O$	Crystalline	$354.1 + 71n$	$n \geqslant 0$	$tCaO \cdot mAl_2O_3$	Vitreous	$166.8t + 361.9m$	$t > 0$ $m \geqslant 0$ $n \geqslant 0$
$Ca(C_2H_3O_2)_2 \cdot nH_2O$	Solution	$362.5 + 71n$	$n \geqslant 0$	$tCaO \cdot mAl_2O_3 \cdot nSiO_2$	Crystalline	$166.8t + 373.6m + 214.6n$	$t > 0$ $n \geqslant 0$
$Ca(C_2H_3O_3)_2 \cdot nH_2O$	Crystalline	$439.1 + 71n$	$n \geqslant 0$	$tCaO \cdot mAl_2O_3 \cdot nFeO_3$	»	$166.8t + 373.6m - 170.2n$	$m \geqslant 0$
$Ca(C_2H_3O_3)_2 \cdot nH_3O$	Solution	$440 + 71n$	$n \geqslant 0$	$CaCl_2 \cdot 2MgCl_2 \cdot nH_2O$	»	$561 + 71n$	$n \geqslant 0$
$Ca(C_2H_5O_2)_2 \cdot mC_2H_5OH$	Crystalline	$230 + 69.05m$	$m \geqslant 0$				

Compound	State	$-\Delta H_f^0$ (in kcal/ mole)	$-\Delta Z_f^0$ (in kcal/ mole)	log K_f	S^0 (in kcal/ / mole · deg.)	C_p^0 (in cal/ / mole · deg.)	n; m; t
$CaSO_3 \cdot nH_2O$	Crystalline	$279 + 71n$	$260.3 + 56.89n$	$190.81 + 41.702n$	$24.3 + 9.866n$	$20.7 + 10.99n$	$n \geqslant 0$
$CaSO_4 \cdot nH_2O$	»	$341.1 + 71n$	$315.41 + 56.89n$	$231.186 + 41.702n$	$26.6 + 9.866n$	$22.5 + 10.99n$	$n \geqslant 0$
$CaS_2O_3 \cdot nH_2O$	»		$260.86 + 56.89n$	$191.188 + 41.702n$			$n \geqslant 0$
$Ca(NO_3)_2 \cdot nCa(OH)_2 \cdot nH_2O$	»	$224.2 + 239.4m + 71n$	$178.33 + 56.89n$	$130.704 + 41.702n$	$44.4 + 9.866n$	$35.7 + 10.99n$	$m \geqslant 0$
$Ca(NO_3)_2 \cdot nH_2O$ [1]	»	$225.4 + 71n$	$178.9 + 56.89n$	$131.152 + 41.702n$	$41.5 + 9.866n$		$n \geqslant 0$
$CaHPO_4 \cdot nH_2O$	»	$434 + 71n$	$400.8 + 56.89n$	$293.8 + 41.702n$	$20.3 + 9.866n$		$n \geqslant 0$
$CaHAsO_4 \cdot nH_2O$	»	$339 + 71n$	$306.1 + 56.89n$	$224.4 + 41.702n$	$25.1 + 9.866n$		$n \geqslant 0$
$CaC_2O_4 \cdot nH_2O$	»	$328.4 + 71n$	$304.42 + 56.89n$	$223.13 + 41.702n$	$27.3 + 9.866n$	$25.4 + 10.99n$	$n \geqslant 0$
$tCaO \cdot mB_2O_3 \cdot nH_2O$	»	$166.8t + 318.1m + 71n$	$158.3t + 301.6m + 56.89n$	$116.18t + 221.06m + 41.702n$	$9.2t + 16.3m + 9.866n$	$9.7t + 15.68m + 10.99n$	$t > 0$ $m \geqslant 0$ $n \geqslant 0$

• The formula and corresponding data refer to modification II.

TABLE 4

Heats of Formation, Free Energies, Equilibrium Constants of Formation Reactions, Entropies and Heat Capacities of Calcium Halides at 25°C

Compound	State	$-\Delta H_f^0$ (in kcal/mole)	$-\Delta Z_f^0$ (in kcal/mole)	log K_f	S^0 (in cal/mole · deg)	C_p^0 (in cal/mole · deg)
CaH_2	Crystalline	(45.1)*	(35.8)*	(26.24)*	(10)*	
CaF_2	»	(290.3)*	(277.7)*	(203.55)*	(16.46)*	(16.02)*
$CaCl_2$	»	(190.0)*	(179.3)*	(131.42)*	(27.2)*	(17.36)*
$CaBr_2$	»	(161.3)*	(156.8)*	(114.93)*	(31)*	
CaI_2	»	(127.8)*	(126.6)*	(92.80)*	(34)*	
CaHF	»	167.7	156.8	114.90	13.2	
CaHCl	»	117.6	107.6	78.83	18.6	16.69
CaHBr	»	103.2	96.3	70.58	20.5	
CaHI	»	86.4	81.2	59.52	22.0	
CaFCl	»	240.2	228.5	167.48	21.83	
CaFBr	»	225.8	217.2	159.24	23.73	
CaFI	»	209.0	202.2	148.18	25.23	
CaClBr	»	175.6	168.0	123.18	29.10	
CaClI	»	158.9	153.0	112.11	30.60	
CaBrI	»	144.6	141.7	103.86	32.5	
CaF_2	Standard solution	(287.09)*	(264.34)*	(193.758)*	(−17.8)*	
$CaCl_2$	»	(209.82)*	(194.88)*	(142.844)*	(13.1)*	
$CaBr_2$	»	(187.57)*	(181.33)*	(132.912)*	(25.4)*	
CaI_2	»	(156.51)*	(156.88)*	(114.991)*	(39.1)*	
CaFCl	»	248.46	229.61	168.301	−2.35	
CaFBr	»	237.33	222.84	163.335	3.80	
CaFI	»	221.80	210.61	154.374	10.65	
CaClBr	»	198.70	188.10	137.878	19.25	
CaClI	»	183.16	175.88	128.918	26.10	
CaBrI	»	172.04	169.10	123.952	32.25	

TABLE 5

Heats of Formation of Calcium Compounds in the Solid State at 25° C

Compound	$-\Delta H_f^0$ (in kcal/ mole)	Compound	$-\Delta H_f^0$ (in kcal/mole)	Compound	$-\Delta H_f^0$ (in kcal/ mole)
$Ca(C_2H_3O_2)_2$	(355.0) 354.	$CaCl_2 \cdot NH_3$	(217.3) 235.	$CaO \cdot Al_2O_3 \cdot 6\,SiO_2$	(1828)*
$Ca(C_2H_3O_2)_2 \cdot H_2O$	(425.1)*	$CaCl_2 \cdot 2NH_3$	(242.8) ~ 254.		
$Ca(C_2H_3O_3)_2$	(441.0) ~ 439.		—	$3CaO \cdot Al_2O_3 \cdot 2SiO_2$	(1303)*
$Ca(C_2H_3O_3)_2 \cdot 5H_2O$	(789.4) 794.	$CaCl_2 \cdot 4NH_3$	(285.0) 292	$CaBr_2 \cdot 2Hg(CN)_2 \cdot 6H_2O$	482
$Ca(C_2H_5O)_2$	(227.1) ~ 230			$CaBr_2 \cdot 2Hg(CN)_2 \cdot 7H_2O$	(553.1)
$Ca(C_2H_5O)_2 \cdot 2C_2H_5O$	(368.2)*	$CaCl_2 \cdot 8NH_3$	(368.5)*	$CaI_2 \cdot 2PbI_2$	(223.1) ~ 216
$CaCl_2 \cdot 2CaO$	(505) ? ~ 531	$CaBr_2 \cdot NH_3$	(189.6) ~ 216.	$CaI_2 \cdot 2PbI_2 \cdot 7H_2O$	(712.6)*
$CaCl_2 \cdot 3CaO$	(654) ? 698	$CaBr_2 \cdot 2NH_3$	(217.1) ~ 235	$CaCl_2 \cdot 2Hg(CN)_2 \cdot 6H_2O$	(501.0)*
$CaCl_2 \cdot 3CaO \cdot 3H_2O$	(910.6)*	$CaBr_2 \cdot 6NH_3$	(307.3) ~ 311	$Ca(NO_3)_2 \cdot Ca(OH)_2$	(461.7) 463.6
$CaCl_2 \cdot 3CaO \cdot 16H_2O$	(1833) 1833.55	$CaBr_2 \cdot 8NH_3$	(349.0)*	$3CaO \cdot Al_2O_3 \cdot 6H_2O$	(1329) 1300
$CaBr_2 \cdot 6H_2O$	(700.7) ? 600	$CaI_2 \cdot NH_3$	(157.7) ~ 183	$4CaO \cdot Al_2O_3$	(1026) 1041
$CaBr_2 \cdot 3CaO \cdot 16H_2O$	(1810)*	$CaI_2 \cdot 2NH_3$	(186.9) ~ 202	$12CaO \cdot 7Al_2O_3$	(4617)*
$CaJ_2 \cdot 8H_2O$	(700.7) ? 710.6	$CaI_2 \cdot 3NH_3$	~ 221	$CaO \cdot Al_2O_3$ (стекл.)	(545) ~ 529

TABLE 5 (continued)

Compound	$-\Delta H_f^0$ (in kcal/ mole)	Compound	$-\Delta H_f^0$ (in kcal/ mole)	Compound	$-\Delta H_f^0$ (in kcal/ mole)
$Ca(NO_3)_2 \cdot Ca(OH)_2 \cdot 2^1/_2H_2O$	(641)*	$CaI_2 \cdot 4NH_3$	~ 240	$2CaO \cdot Al_2O_3$ (стекл.)	(695)*
CaO_2	(157.5)	$CaI_2 \cdot 5NH_3$	~ 259	$Ca(H_2PO_4)_2$	(744.4)
	~ 152				~ 751
$CaO_2 \cdot 8H_2O$	(719.7)*	$CaI_2 \cdot 6NH_3$	(285.3)	$Ca(H_2PO_4)_2 \cdot H_2O$	(818)
			278		822
$CaCl_2 \cdot H_2O$	(265.1)	$CaI_2 \cdot 7NH_3$	297		
	~ 268				
		$CaI_2 \cdot 8NH_3$	(316.1)*	$Ca(H_2PO_4)_2 \cdot H_2O \cdot NH_3$	(840.6)
					841
$CaCl_2 \cdot 2H_2O$	(335.5)	$2CaO \cdot Al_2O_3$	(704)	$Ca(H_2PO_4)_2 \cdot H_2O \cdot 2NH_3$	(860.7)
	~ 339		(708)		860
$CaCl_2 \cdot 4H_2O$	(480.2)	$2CaO \cdot Al_2O_3 \cdot 5H_2O$	1078	$Ca(H_2PO_4)_2 \cdot H_2O \cdot 3NH_3$	879
	481		(1063)		
$CaCl_2 \cdot 6H_2O$	(623.15)*	$2CaO \cdot Al_2O_3 \cdot 6H_2O$	1134	$Ca(H_2PO_4)_2 \cdot H_2O \cdot 4NH_3$	(898.0)

TABLE 6

Heats, Free Energies and Equilibrium Constants of Formation Reactions, Entropies and Heat Capacities of Calcium Compounds in the Crystalline State at 25° C

Compound	$-\Delta H_f^0$ (in kcal/ mole)	$-\Delta Z_f^0$ (in kcal/ mole)	log K_f	S^0 (in cal/ mole · deg.)	C_p^0 (in cal/ mole · deg)
				(24.2)	(21.90)
$CaSO_3$	~ 279	~ 260	~ 190.8	24.3	20.7
$CaSO_3 \cdot 2H_2O$	(421.2)*	(374.1)*	(274.21)*	(44)*	(42.7)*
$CaSO_4$	(342.42)	(315.56)	(231.301)	(25.5)	(23.8)
	341.06	315.41	231.186	26.6	22.5

TABLE 6 (continued)

Compound	$-\Delta H_f^0$ (in kcal/ mole)	$-\Delta Z_f^0$ (in kcal/ mole)	log K_f	S^0 (in cal/ mole · deg)	C_p^0 (in cal/ mole · deg)
$CaSO_4 \cdot {}^1/_2H_2O$	(376.47) 376.56	(343.02) 343.86	(251.429) 252.04	(31.2) 31.56	(28.6) 28
$CaSO_4 \cdot H_2O$	412.1	386.4	272.89	36.5	33.5
$CaSO_4 \cdot 2H_2O$	483.06	457.4	314.59	46.36	44.5
$CaO \cdot B_2O_3$	(483.3) 484.9	(457.7) 460.	(335.49) 337.2	(25.1) 25.5	 25.4
$CaO \cdot 2B_2O_3$	(798.8) ~ 803.	(752.4) ~ 762	(551.50) ~ 558	(32.2) ~ 41.8	(37.75) ~ 41
$2CaO \cdot B_2O_3$	(651.6) *	(618.6) *	(453.42) *	(34.7) *	(35.16) *
$3CaO \cdot B_2O_3$	(817.7) * 818.	(777.1) *	(569.60) *	(43.9) *	(44.90) *
$CaC_2O_4 \cdot H_2O$	(400.4) 400.	(361.9) 361.3	(265.27) 264.83	(37.28) 37.13	 (36.4)
$CaC_2O_4 \cdot 2H_2O$	(470.4) *	(418.2) *	(306.53)	(47.) *	47
$CaHPO_4$	(435.2) 434.	(401.5) 401	(294.29) 294.	(21) 20	 —
$CaHPO_4 \cdot 2H_2O$	(576) *	(514.6) *	(377.19) *	(40.) *	—
$Ca(NO_3)_2$	(224.00) 224.18	(177.34) 178.33	(129.988) 130.704	(46.2) 44.4	 35.69
$Ca(NO_3)_2 \cdot H_2O$	295	235	172.41	54.3	—
$Ca(NO_3)_2 \cdot 2H_2O$	(368)	(293.51)	(215.139)	(64.3)	—
$Ca(NO_3)_2 \cdot 3H_2O$	(437.18)	(349.0) *	(255.81) *	(74.) *	—

as correct starting values; these are marked with stars in the tables. The general approximate formulas for all the families are given in Table 1. Table 2 gives the heats of formation we calculated for a series of mixed halides of gallium, indium and thallium in the crystalline state and for their solutions in HCl or water. The calculations were based on data from [5 – 7]. In addition to this, we determined the heats of formation of the complexes $[Tl(H_2O)_4]Cl_2Br$ and $[Tl(H_2O)_4]ClBr_2$, starting from the heats of formation of $[Tl(H_2O)_4]Cl_3$ and $[Tl(H_2O)_4]Br_3$, reported by K. B. Yatsimirskii [11]. For comparison, we also present available information from other sources [5 – 11]; data from paper [5] are in round brackets.

The accuracy of our calculations depends on the accuracy of the starting data [5 – 11]. If we accept the latter as true values, then for halogen derivatives containing Ga, In and Tl, the average accuracy of the calculations was 0.1 – 0.5% and for the thermodynamic properties of ammoniates and crystal hydrates, calculated by method [2], of the order of 0.5 – 1%. For crystal hydrates (Table 2), the error of our calculations was approximately 0.5 – 1% and rarely, 1 – 2%. The accuracy of the calculations of the thermodynamic properties for ammoniates was, on an average, of the order of 0.5 – 5%; however, for the first representatives with $m < 4$, the errors in the calculations could reach 10 – 15%.

Then, by the method indicated [2], we calculated some thermodynamic characteristics of mixed halides of calcium (Table 4) in the crystalline state and partly in standard solution (in HCl or H_2O).

Finally, from formula (1) we found approximate general expressions for determining the thermodynamic properties of a series of families of crystal hydrates, ammoniates and other compounds containing calcium (Table 3). In Tables 5 and 6, the results of calculations for a large group of compounds are compared with experimental data from [5]; the latter are given in round brackets and some of them, used as starting data, are marked with a star. As Tables 5 and 6 show, our results are in satisfactory agreement with experiment [5].

On the whole, the possible errors in the values of the thermodynamic properties calculated from the formulas in Table 3 are of the order of 0.2 – 1%. In addition, their accuracy also depends on the degree of accuracy of the starting values in [5].

The great difference between the calculated and experimental values of the heat of formation of the crystal hydrate $CaBr_2 \cdot 6H_2O$ (600 kcal/mole instead of 700.7, Table 5) is evidently explained by an error in [5]. This is readily understood from an analysis of the data presented in Tables 5 and 6. For example, according to our method [2], $-\Delta H_f^\circ$ for $CaI_2 \cdot 8H_2O$ equals 710.6 kcal/mole and according to data in [5] it is 700.7 kcal/mole, i.e. the difference is 1.4%; similarly, for $CaCl_2 \cdot 3CaO \cdot 16H_2O$, $CaSO_4 \cdot \frac{1}{2}H_2O$, $CaSO_4$, $CaBr_2 \cdot 6NH_3$ and $Ca(NO_3)_2 \cdot 2H_2O$ our calculations of the heat of formation ($-\Delta H_f^\circ$, kcal/mole) at 25° C gave 1833.55, 376.56, 341.06, 311 and 366, while according to data in [5], the values are 1833, 376.47, 342.42, 307.3 and 368, respectively, and the differences are only 0.1, 0.03, 0.4, 1.2 and 0.6% so that better agreement can hardly be expected. There is approximately the same order of agreement in other cases (see Tables). Without doubt, the heats of formation of the crystalline compounds $CaCl_2 \cdot 2CaO$ and $CaCl_2 \cdot 3CaO$, given in [5] (see also Table 4), are quite low. Our data are more reliable values.

For all the compounds, the formulas given in Tables 1 and 3 are published for the first time; we consider that they may be found useful in various practical problems.

SUMMARY

1. Approximate formulas were obtained for determining the heats of formation, free energies, logarithms of the equilibrium constants of the formation reactions, entropies and heat capacities at 25° C for calcium, gallium, indium and thallium compounds in the crystalline state and partly in solution (in HCl and H_2O).

2. The thermodynamic properties of a series of compounds of calcium, gallium, indium and thallium were calculated by the method described in [1 and 2] and by the formulas mentioned above.

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PHYSICOCHEMICAL INVESTIGATION OF THE INTERACTION OF ZIRCONIUM HALIDES WITH ESTERS OF MONOBASIC ACIDS IV. COMPLEXES OF ZIRCONIUM BROMIDE

Yu. B. Kletenik and O. A. Osipov

Novocherkassk Polytechnical Institute

The different capacities of chlorides of elements of group IV for forming complexes with organic addends is conveniently explained from the point of view of the shielding of the acceptor atom by chlorine atoms. As some literature data [1, 2] show, in the series of silicon, germanium and tin chlorides, there is a growth in the complex-forming capacity, which corresponds to the increase in the ratio $\frac{r_{Me}}{r_{Hal}}$ and the decrease in the degree of shielding of the central atom. A similar rule was observed for complexes of $TiCl_4$ and $ZrCl_4$ with dioxane [3]. The effect of the steric factor $\frac{r_{Me}}{r_{Hal}}$ on the complex-forming capacity of metal halides may also be followed by comparing the physicochemical properties of complexes formed by different halides of the same element with the same addends. There has been very little study of the change in the complex-forming properties of halides of group IV elements in the series chloride — bromide — iodide. It was reported [4] that for tin, the stability of the complexes decreased in going from $SnCl_4$ to $SnBr_4$. The change in the polar properties of complexes in this series has not been studied.

Previously, we investigated the polar properties of zirconium chloride complexes with a series of esters of monobasic acids [5 — 7]. The present work is devoted to a study of complexes formed by zirconium bromide with the same esters by means of dielectric permeability and cryoscopy in benzene and also by preparative isolation.

The procedure for investigation and purfication of the reagents used in the work was described previously [3, 5]. In determining the increase in the dipole moment due to the formation of the coordination bond, it was assumed that the dipole moment of $ZrBr_4$ itself was equal to zero. The basis for this was data on the tetrahedral structure and the nonpolarity of all the tetrahalides of group IV elements studied [8, 9].

Zirconium bromide does not dissolve in benzene. Thus, after prolonged shaking of $ZrBr_4$ in carefully dried benzene, dissolved bromide could not be detected in the latter. The solutions investigated were prepared by dissolving $ZrBr_4$ in benzene containing exactly the calculated amount of ester. The whole of the zirconium bromide only dissolved when the amount of ester in the benzene was not less than that required for the formation of a complex of the composition $ZrBr_4 \cdot E$, which indicates the existence of complexes of this type in benzene. Benzene solutions of zirconium bromide complexes with esters had a yellow color and fumed strongly in air (the result of hydrolysis). In their preparation and investigation, all measures were taken to prevent their contact with atmospheric moisture.

Tables 1 — 3 give the dielectric permeabilities, densities and molecular polarizabilities of the complexes $ZrBr_4 \cdot HCOOC_2H_5$, $ZrBr_4 \cdot CH_3COOC_2H_5$ and $ZrBr_4 \cdot C_3H_7COOC_2H_5$ in benzene.

The dipole moments of these complexes (μ), the dipole moments of the esters forming part of them (μ_1) and the differences between them ($\mu - \mu_1$) are given in Table 4. For comparison, the values of the differences ($\mu - \mu_1$) for analogous complexes of zirconium chloride are given in the last column.

TABLE 1

Complex $ZrBr_4 \cdot HCOOC_2H_5$ in benzene, P_∞ = 500 cm³, R = 69.0 cm³, μ = 4.50 D

c	ε_{12}	d_4^{20}	P_{CC}
0.00753	2.406	0.9052	278
0.00491	2.373	0.8961	298
0.00390	2.358	0.8925	307
0.00303	2.346	0.8893	323
0.00254	2.340	0.8876	340
0.00186	2.331	0.8850	377

TABLE 2

Complex $ZrBr_4 \cdot CH_3COOC_2H_5$ in benzene, P_∞ = 290 cm³, R = 73.3 cm³, μ = 3.15 D

c	ε_{12}	d_4^{20}	P_{CC}
0.00502	2.330	0.8958	181
0.00419	2.328	0.8928	197
0.00358	2.324	0.8907	204
0.00296	2.320	0.8887	213
0.00218	2.314	0.8859	227
0.00141	2.308	0.8833	252

TABLE 3

Complex $ZrBr_4 \cdot C_3H_7COOC_2H_5$ in benzene, P_∞ = 360 cm³, R = 82.6 cm³, μ = 3.57 D

c	ε_{12}	d_4^{20}	P_{CC}
0.00432	2.343	0.8913	267
0.00359	2.337	0.8891	279
0.00282	2.330	0.8869	294
0.00233	2.324	0.8854	301
0.00189	2.319	0.8841	313
0.00142	2.313	0.8827	325

The data obtained indicate that the formation of complexes of $ZrBr_4$ with esters of monobasic acids, with the composition $ZrBr_4 \cdot E$, is accompanied by the development of a strongly polarized coordination bond. As the data presented show, no definite rule was observed in the change in polarity of complexes of this composition in going from $ZrCl_4$ to $ZrBr_4$.

The figure shows data from cryoscopic measurements on the complexes $ZrBr_4 \cdot HCOOC_2H_5$ and $ZrBr_4 \cdot CH_3COOC_2H_5$ in benzene. Here, the concentrations are expressed in mole fractions for convenience in comparing these data with the values of the dielectric polarization of the same complexes. The results of the cryoscopic measurements indicate a tendency for the complexes with the composition $ZrBr_4 \cdot E$ to dimerize, but this is shown much more weakly than by the analogous complexes of zirconium chloride [6].

TABLE 4

Complex	μ	μ_1	$\mu - \mu_1$	$\mu - \mu_1$ for complexes with $ZrCl_4$
$ZrBr_4 \cdot HCOOC_2H_5$	4.50	1.92	2.58	2.23
$ZrBr_4 \cdot CH_3COOC_2H_5$	3.15	1.81	1.34	2.08
$ZrBr_4 \cdot C_3H_7COOC_2H_5$	3.57	1.74	1.83	1.79

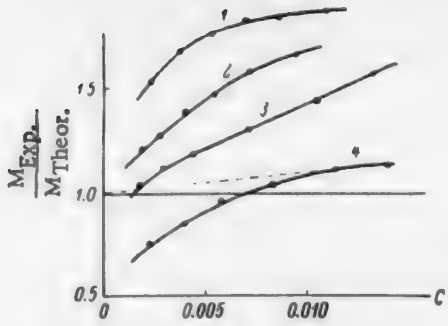
Tables 5 – 9 give data on the dielectric polarization of the complexes $ZrBr_4 \cdot 2HCOOC_2H_5$, $ZrBr_4 \cdot 2CH_3COOC_2H_5$, $ZrBr_4 \cdot 2CH_3COOC_3H_7$, $ZrBr_4 \cdot 2CH_3COOC_4H_9$ and $ZrBr_4 \cdot 2C_3H_7COOC_2H_5$.

For the complex with ethyl formate, the addition of the second molecule of ester to $ZrBr_4$ is accompanied by a considerable growth in polarity in comparison with the polarity of the complex $ZrBr_4 \cdot HCOOC_2H_5$. The character of the dependence of the molecular polarization P on the concentration indicates the relative stability of the complex $ZrBr_4 \cdot 2HCOOC_2H_5$. Noticeable dissociation into the components only occurs at very low concentrations. The dipole moment of this complex, μ = 7.85 D is very close to the dipole moment of the complex $ZrCl_4 \cdot 2HCOOC_2H_5$ (μ = 7.63 D).

TABLE 5

Complex $ZrBr_4 \cdot 2HCOOC_2H_5$ in benzene, P_∞ = 1380 cm³, R = 87.1 cm³, μ = 7.85 D

c	ε_{20}	d^{20}_4	P cc
0.01021	3.313	0.9159	1274
0.00678	2.955	0.9036	1324
0.00512	2.786	0.8976	1348
0.00378	2.650	0.8925	1361
0.00300	2.573	0.8896	1369
0.00228	2.501	0.8870	1362



Determination of the molecular state of zirconium bromide complexes in benzene solutions. 1) $ZrBr_4 \cdot HCOOC_2H_5$, 2) $ZrBr_4 \cdot CH_3COOC_2H_5$, 3) $ZrBr_4 \cdot 2HCOOC_2H_5$, 4) $ZrBr_4 \cdot 2CH_3COOC_2H_5$.

The character of the dependence of the molecular polarization on concentration for the complexes $ZrBr_4 \cdot 2CH_3COOC_2H_5$, $ZrBr_4 \cdot 2CH_3COOC_3H_7$ and $ZrBr_4 \cdot 2CH_3COOC_4H_9$ indicates their dissociation in solution.

The figure shows the results of cryoscopic investigations of the complexes $ZrBr_4 \cdot 2HCOOC_2H_5$ and $ZrBr_4 \cdot 2CH_3COOC_2H_5$. At concentrations below 0.0070 mole fraction, the complex with ethyl acetate has a ratio of $\frac{M_{Exp}}{M_{Theor}} < 1$, which indicates the predominance of decomposition processes (removal of an ester molecule) over association*.

Data presented above for complexes of the composition $ZrBr_4 \cdot E$ indicates the absence of noticeable dissociation of these complexes into the components. This conclusion is supported by the fact that quite transparent benzene solutions are formed, containing zirconium bromide and ester in a ratio of 1 : 1. In the case of noticeable dissociation of complexes with the composition $ZrBr_4 \cdot 2E$ into components, the benzene-insoluble zirconium bromide would have separated as a precipitate and this was not observed. Thus, the most probable dissociation scheme for complexes of composition $ZrBr_4 \cdot 2E$ in benzene is the following: $ZrBr_4 \cdot 2E \rightleftharpoons ZrBr_4 \cdot E + E$.

We proposed a similar dissociation scheme for zirconium chloride complexes with esters of the composition $ZrCl_4 \cdot 2E$ [7].

TABLE 6

Complex $ZrBr_4 \cdot 2CH_3COOC_2H_5$ in benzene, P_∞ = 350 cm³, R = 95.6 cm³, μ = 3.40 D

c	ε_{20}	d_4^{20}	P cc
0.01032	2.636	0.9167	545
0.00683	2.498	0.9040	513
0.00511	2.434	0.8976	496
0.00416	2.399	0.8939	461
0.00339	2.374	0.8911	442
0.00257	2.350	0.8879	425

TABLE 7

Complex $ZrBr_4 \cdot 2CH_3COOC_3H_7$ in benzene, P_∞ = 440 cm³, R = 98.6 cm³, μ = 3.97 D

c	ε_{20}	d_4^{20}	P cc
0.01137	2.741	0.9208	629
0.00701	2.544	0.9148	599
0.00527	2.470	0.8983	576
0.00411	2.425	0.8942	559
0.00331	2.394	0.8910	542

* The electroconductivity of these solutions was very low (not more than 10^{-7} ohm^{-1} cm^{-1}) so that the effect of electrolytic dissociation on the apparent molecular weight of the complex is practically excluded.

TABLE 8

Complex $ZrBr_4 \cdot 2CH_3COOC_4H_9$ in benzene, P_∞ = 500 cm³, R = 114.0 cm³, μ = 4.21 D

c	ε_{20}	d_4^{20}	P cc
0.01129	2.787	0.9198	696
0.00663	2.554	0.9044	670
0.00516	2.487	0.8974	644
0.00432	2.451	0.8972	636
0.00297	2.393	0.8893	604
0.00188	2.350	0.8853	573

TABLE 9

Complex $ZrBr_4 \cdot 2C_3H_7COOC_2H_5$ in benzene, P_∞ = 430 cm³, R = 114.2 cm³, μ = 3.80 D

c	ε_{20}	d_4^{20}	P cc
0.01110	2.528	0.9195	408
0.00756	2.441	0.9065	391
0.00542	2.390	0.8987	370
0.00401	2.358	0.8933	351
0.00297	2.340	0.8895	350
0.00251	2.334	0.8879	359
0.00182	2.324	0.8853	376

TABLE 10

Complex $ZrBr_4 \cdot 2CH_3COOC_2H_5$ in benzene with excess ethyl acetate

c_1	c_2	ε_{20}	d_4^{20}	P cc
$ZrBr_4$: ethyl acetate = 1 : 3, P_∞ = 450 cc				
0.00627	0.00627	2.527	0.9023	547
0.00417	0.00417	2.441	0.8943	532
0.00311	0.00311	2.399	0.8903	521
0.00227	0.00227	2.367	0.8871	507
$ZrBr_4$: ethyl acetate = 1 : 5, P_∞ = 500 cc				
0.00662	0.01986	2.607	0.9036	549
0.00505	0.01515	2.526	0.8976	543
0.00360	0.01080	2.454	0.8921	535
0.00238	0.00714	2.396	0.8876	526
$ZrBr_4$: ethyl acetate = 1 : 7, P_∞ = 515 cc				
0.00711	0.03555	2.704	0.9053	550
0.00504	0.02520	2.577	0.8676	549
0.00336	0.01680	2.476	0.8912	542
0.00249	0.01245	2.426	0.8880	537

The compex character of the dependence of molecular polarization P on concentration for the complex $ZrBr_4 \cdot 2C_3H_7COOC_2H_5$ (Table 9) may be explained in the following way. At low concentration of complex in solution (below 0.003 mole fraction), the zirconium bromide hardly reacts with the second molecule of ethyl butyrate and the fall in polarization with an increase in concentration is produced by association of the complex $ZrBr_4 \cdot C_3H_7COOC_2H_5$. With a further increase in concentration, the equilibrium is shifted toward the formation of the more polar complex $ZrBr_4 \cdot 2C_3H_7COOC_2H_5$, which leads to an increase in the value of P.

Comparison of the data presented above for complexes of zirconium bromide with acetates and ethyl butyrate, of the composition $ZrBr_4 \cdot 2E$, with data obtained previously for complexes of the composition $ZrCl_4 \cdot 2E$ [5, 7] leads to the conclusion that in going from $ZrCl_4$ to $ZrBr_4$, the tendency of the complexes for dissociation by the scheme presented above increases. For a more definite quantitative characterization of this rule, we attempted to calculate the approximate value of the dissociation constant of the complex $ZrBr_4 \cdot 2CH_3COOC_2H_5$, starting from data on its molecular polarization and cryoscopic measurements.

Table 10 shows data on the molecular polarization of the complex $ZrBr_4 \cdot 2CH_3COOC_2H_5$ in benzene solutions, containing various excesses of ethyl acetate in comparison with the amount required for formation of the

complex. The letters c_1 and c_2 denote the concentrations of the complex $ZrBr_4 \cdot 2CH_3COOC_2H_5$ and free ester, expressed in mole fractions. The polarization of the complex was calculated, starting from the composition of $ZrBr_4 \cdot 2CH_3COOC_2H_5$. The polarization of the excess free ethyl acetate was taken as equal to 94 *. From the total polarization of the solution, we deducted the value $94 \cdot c_2$, i.e. the contribution to the polarization from the excess ester.

The increase in the polarization of the complex with an increase in the excess ester indicates suppression of dissociation of the complex into components.

The values of P_∞ for the complex with various excesses of ethyl acetate were extrapolated to an infinitely great excess of ethyl acetate and we obtained the value $P_{comp} = 530$ cm^3, which may be considered as approximately the polarization of the complex $ZrBr_4 \cdot 2CH_3COOC_2H_5$ itself. The dipole moment of the complex, corresponding to this polarization value, equals 4.50 D.

We assume that zirconium bromide reacts with only two molecules of ester. We previously showed that in benzene, zirconium bromide reacts with not more than two molecules of ester [7]. Considering that in going from zirconium chloride to the bromide, even the bond with the second ester molecule is considerably weakened, it is unlikely that zirconium bromide reacts with more than two molecules of ethyl acetate.

Knowing the polarization of the complex $ZrBr_4 \cdot 2CH_3COOC_2H_5$ ($P_{comp} = 530$ cm^3), its polarization with complete elimination of one ester molecule ($P_\infty = 250$ cm^3) and its polarization in solutions of definite, low concentration (P_c), we may calculate the degree of dissociation (α) and the dissociation constant (K) of this complex in benzene:

$$\alpha = \frac{P_{comp} - P_c}{P_{comp} - P_\infty}; \quad K = \frac{c\alpha^2}{1-\alpha},$$

where c is the molar concentration of the complex. For the fifth and sixth solutions in Table 6 we obtained $\alpha_5 = 0.49$ and $\alpha_6 = 0.58$; $K_5 = 1.8 \cdot 10^{-2}$, $K_6 = 2.3 \cdot 10^{-2}$, $K_{av} \approx 2 \cdot 10^{-2}$.

We also calculated the dissociation constant of the complex $ZrBr_4 \cdot 2CH_3COOC_2H_5$ from cryoscopic data, assuming that in the absence of dissociation into components, the course of the cryoscopic curve would have been that indicated by dots in the figure and that at complete dissociation (elimination of one ester molecule), the ratio $\frac{M_{exp}}{M_{theor}}$ would equal 0.5.

For a solution of the complex $ZrBr_4 \cdot 2CH_3COOC_2H_5$ (0.00225 mole fraction) we obtained the values $\alpha = 0.52$ and $K = 1.4 \cdot 10^{-2}$. Considering the difficulty of obtaining accurate data for dilute solutions and the approximate nature of the calculation itself (no allowance was made for association of the complex $ZrBr_4 \cdot 2CH_3COOC_2H_5$, formed as a result of dissociation of the original complex), we can consider such agreement of the K values as satisfactory. For the complex $ZrCl_4 \cdot 2CH_3COOC_2H_5$, we previously [7] obtained a K value of about $5 \cdot 10^{-4}$, i.e. approximately 2 orders less.

Thus, for complexes $ZrHal_4 \cdot 2CH_3COOC_2H_5$, the change from zirconium chloride to the bromide leads to an increase in the dissociation by the scheme presented above and a fall in polarity. The tendency of complexes of the composition $ZrHal_4 \cdot E$ for dimerization falls in the same direction. In our opinion, this confirms the truth of the hypothesis put forward previously [6] that the tendency of complexes of this composition for dimerization is caused by their coordination unsaturation.

In previous work, we established that the alcohol residue of the esters had hardly any effect on the polarity of the complexes of these esters with zirconium chloride [5]. One of us noted the same phenomenon for the complexes of $TiCl_4$ and $SnCl_4$ with esters [12]. Starting from ideas on steric hindrance, which increases on going from $ZrCl_4$ to $ZrBr_4$, it might be surmised that an increase in the alcohol residue would lead to a decrease in the

* We obtained this value by measuring the polarity of ethyl acetate in benzene; it agrees well with literature data [10, 11]. We neglected the slight change in this value with the change in ethyl acetate concentration.

polarity of the comples. Meanwhile, a comparison of data on the polarity of the complexes $ZrBr_4 \cdot 2CH_3COOC_2H_5$, $ZrBr_4 \cdot 2CH_3COOC_3H_7$ and $ZrBr_4 \cdot 2CH_3COOC_4H_9$ (Tables 6 – 8) leads to the somewhat unexpected conclusion that the polarity of the complexes increases with an increase in the alcohol residue. According to our previous data, a similar rule is observed for complexes of ZrI_4 with esters of monobasic acids. It is possible that this rule is caused by dispersion interaction between the zirconium halide molecule and the hydrocarbon radical. While it is insignificant in the case of chlorine, this interaction may increase noticeably in going to the more readily polarizable bromine.

We carried out a preparative isolation of zirconium bromide complexes with esters of the composition $ZrBr_4 \cdot E$. The procedure for preparing these complexes was as follows. Zirconium bromide was shaken for a long period with a small volume of benzene, containing the ester in the stoichiometric amount. The $ZrBr_4$ gradually dissolved and the solution deposited crystals of the complex, which were then transferred to a glass filter and dried in a stream of dry air at room temperature. In this way, we obtained the complexes $ZrBr_4 \cdot CH_3COOC_2H_5$ and $ZrBr_4 \cdot C_3H_7COOC_2H_5$. Their melting points were found to be 164 and 157°, respectively, i.e. very close to the melting points of the analogous complexes with zirconium chloride (170 and 163°) [6]. In an attempt to isolate the complex with ethyl formate, we isolated a complex containing bound benzene in its composition. Analysis of this complex for Zr, Br and benzene gave results close to the formula $ZrBr_4 \cdot HCOOC_2H_5 \cdot C_6H_6$. When the complex had been dried for 5 hours in a stream of dry air at room temperature, the benzene in it was found to be 70% of theoretical. When the complex was heated, the benzene was eliminated without it melting. Thus, when heated to 50° in a stream of dry air for 30 minutes, the complex completely lost the benzene. Analysis of such a benzene-free complex for Zr and Br gave results, which corresponded to the formula $ZrBr_4 \cdot HCOOC_2H_5$ within the limits of ± 1%. This compound melted at 108°. From what has been said, it may be concluded that in the complex $ZrBr_4 \cdot HCOO \cdot C_2H_5C_6H_6$, the benzene is bound considerably more weakly than in the complex $ZrCl_4 \cdot HCOOC_2H_5 \cdot C_6H_6$, studied previously [6].

SUMMARY

The dipole moments of the complexes $ZrBr_4 \cdot HCOOC_2H_5$, $ZrBr_4 \cdot CH_3COOC_2H_5$, $ZrBr_4 \cdot C_3H_7COOC_2H_5$, $ZrBr_4 \cdot 2HCOOC_2H_5$, $ZrBr_4 \cdot 2CH_3COOC_2H_5$, $ZrBr_4 \cdot 2CH_3COOC_3H_7$, $ZrBr_4 \cdot 2CH_3COOC_4H_9$ and $ZrBr_4 \cdot 2C_3H_7COOC_2H_5$ were measured.

The complexes $ZrBr_4 \cdot HCOOC_2H_5$, $ZrBr_4 \cdot CH_3COOC_2H_5$, $ZrBr_4 \cdot 2HCOOC_2H_5$, and $ZrBr_4 \cdot 2CH_3COOC_2H_5$ were studied cryosocopically.

For complexes of the composition $ZrBr_4 \cdot 2E$ (with the exception of complexes with ethyl formate) in the zirconium chloride — bromide series, a fall in polarity and an increase in the dissociation of the bond with the second ester molecule was observed. The tendency of complexes of the composition $ZrBr_4 \cdot 2E$ for dimerization was expressed much more weakly than for the analogous complexes of zirconium chloride.

On the basis of data on polarization and cryoscopic measurements on the complex $ZrBr_4 \cdot 2CH_3COOC_2H_5$, its dissociation constant in benzene was calculated and found to equal approximately $2 \cdot 10^{-2}$.

It was established that for complexes of $ZrBr_4$ with ethyl acetate, propyl acetate and isobutyl acetate, an increase in polarity was observed with an increase in the alcohol radical.

The complexes $ZrBr_4 \cdot HCOOC_2H_5$, $ZrBr_4 \cdot CH_3COOC_2H_5$, and $ZrBr_4 \cdot C_3H_7COOC_2H_5$ were isolated preparatively and their melting points determined.

The mixed complex $ZrBr_4 \cdot HCOOC_2H_5 \cdot C_6H_6$ was isolated preparatively. It was established that the benzene was bound considerably more weakly in it than in the analogous complex with zirconium chloride.

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INTERACTION OF STANNIC CHLORIDE WITH ESTERS. I

T. Sumarokova and R. Omarova

Institute of Chemical Sciences, Academy of Sciences, Kazakh, SSR

The complex compounds of stannic chloride with esters of monocarboxylic acids of the composition $SnCl_4 \cdot 2A$ were first described by Pfeiffer and Halperin [1]. Later, N. S. Kurnakov et al. [2 – 6] used physico-chemical analysis methods to study the systems formed by stannic chloride and bromide with esters of monocarboxylic and dicarboxylic acids. N. S. Kurnakov and É. B. Shternina [4] measured the electroconductivity of the $SnCl_4 - CH_3COOC_2H_5$ and $SnBr_4 - CH_3COOC_2H_5$.

The presence of electroconductivity in these systems may be explained, in analogy with carboxylic acids [7 – 13], by the following reactions:

$$SnX_4 + 2RCOOR' \rightleftarrows [SnX_4(RCOO)_2]R'_2 \quad (1)$$

$$[SnX_4(RCOO)_2]R'_2 + RCOOR' \rightleftarrows [SnX_4(RCOO)_2]R'^{-} + RCOOR'^{+}_2 \quad (2)$$

$$[SnX_4(RCOO)_2]R'_2 + 2RCOOR' \rightleftarrows [SnX_4(RCOO)_2]^{--} + 2RCOOR'^{+}_2 \quad (3)$$

Equations 1 – 3 show that the occurrence of electroconductivity in systems formed by stannic chloride and bromide with esters is only possible, in our opinion, with the existence of compounds of the type $SnX_4 \cdot 3A$ and $SnX_4 \cdot 4A$ in these systems. This conclusion stems from the idea that the alkyl cations R^+ are incapable of prolonged independent existence in solutions and are only split off in the presence of a molecule, with which they can combine.

We set ourselves the problem of determining whether stannic chloride and esters formed the compounds $SnCl_4 \cdot 3RCOOR'$ and $SnCl_4 \cdot 4RCOOR'$, i.e. whether the esters dissociated in accordance with equations 1 – 3, and as subjects for the investigation we chose ethyl esters of chlorine-substituted acetic acid; here we started from the following considerations. Replacement of an acid hydrogen by an aliphatic radical does not deprive the molecule of its acid properties but only weakens them [14, 15]. Therefore, it can be considered that esters possess acid properties, but that these properties, i.e. esters' capacity for electrolytic dissociation, are expressed considerably more weakly than those of the corresponding carboxylic acids. However, since the molecules of addends, added to tin, are strongly "acidified", the acidic properties of esters, which are weakly expressed by the free molecules, may be detected more readily when these molecules are added to tetravalent tin. This is also expressed by Equations 1 – 3.

It seemed to us that the accuracy of these ideas could be checked experimentally to some extent by a comparison of the behavior of the system of $SnCl_4$ with the ethyl esters of acetic, monochloroacetic and trichloroacetic acids with the behavior of the corresponding $SnCl_4$ – carboxylic acid systems and with each other.

EXPERIMENTAL

For studying the interaction of stannic chloride with esters, we used physicochemical analysis methods, such as viscosimetry, conductimetry, volumetry and cryoscopy. The working procedures and also the preparation and purification of stannic chloride were described previously [12, 16].

TABLE 1

$SnCl_4$ (mole %)	Viscosity (in centipoises)						$SnCl_4$ (mole %)	B (in kcal)
	20°	50°	60°	70°	90°	100°		
0.00	1.68	1.07	0.931	0.829	0.655	0.593	0	2.82
5.07	—	—	—	—	0.655	0.595	10	2.72
9.43	—	1.05	0.931	0.825	0.657	0.601	20	2.65
15.55	1.59	1.02	0.909	0.816	—	—	30	2.56
17.97	—	—	—	—	0.638	0.585	40	2.47
23.85	1.53	0.979	0.869	0.782	—	—	50	2.34
30.35	—	—	—	—	0.607	0.563	60	2.24
34.76	1.39	0.946	0.806	0.730	—	—	70	2.19
46.10	1.28	0.853	0.756	0.687	0.565	0.525	80	2.12
55.16	1.18	0.795	0.719	0.649	0.543	0.504	90	2.05
66.41	1.08	0.746	0.677	0.623	—	—	100	1.98
74.82	1.02	0.712	0.656	0.600	0.501	0.464		
80.55	0.985	0.706	0.645	0.589	—	—		
90.28	0.930	0.666	0.612	0.560	0.476	0.439		
100.00	0.888	0.630	0.582	0.539	0.463	0.429		

TABLE 2

$SnCl_4$ (mole %)	Density (g/cc)					
	20°	50°	60°	70°	90°	100°
0.00	1.3817	1.3444	1.3208	1.3127	1.2827	1.2684
5.07	—	—	—	—	1.3135	1.2954
9.43	—	1.4100	1.3930	1.3750	1.3474	1.3341
15.55	1.4999	1.4535	1.4380	1.4240	—	—
17.97	—	—	—	—	1.4054	1.3835
23.85	1.5646	1.5169	1.5011	1.4858	—	—
30.35	—	—	—	—	1.4901	1.4736
34.76	1.6470	1.5955	1.5780	1.5599	—	—
46.10	1.7427	1.6834	1.6650	1.6463	1.6100	1.5874
55.16	1.8166	1.7575	1.7381	1.7173	1.6791	1.6574
66.41	1.9214	1.8571	1.8366	1.8156	—	—
74.82	1.9896	1.9224	1.9015	1.8771	1.8367	1.8089
80.55	2.0373	1.9699	1.9468	1.9241	—	—
90.28	2.1300	2.0588	2.0381	2.0078	1.9678	1.9413
100.00	2.2331	2.1566	2.1313	1.1127	2.0493	2.0207

The esters were synthesized from anhydrous alcohol and previously purified acids. The ethyl ester of monochloroacetic acid had b.p. 138.5° at 696 mm and the ethyl ester of trichloroacetic acid, 163.2° at 701 mm.

1. $SnCl_4 - CCl_3COOC_2H_5$ system. When stannic chloride was mixed with ethyl trichloroacetate, no noticeable heat effect was detected. The mixture did not conduct an electric current. Therefore the $SnCl_4 - CCl_3COOC_2H_5$ system was studied by viscosity and density and also by the cryoscopic method.

The results of measuring the viscosity and the calculated values of B, found from the equation $\eta = Ae^{\frac{B}{RT}}$ [17-19], are presented in Table 1; Table 2 gives the results of density measurements. Fig. 1 shows a diagram of properties against composition for the $SnCl_4 - CCl_3COOC_2H_5$ system.

The viscosity isotherms, corresponding to 20, 50, 60 and 70°, appeared as S-shaped curves, which changed into curves with a maximum when the temperature was increased. We observed a clearly expressed maximum on the viscosity isotherm corresponding to 100°. The appearance of a maximum on viscosity isotherms with an increase in temperature is explained by the fact that the viscosity temperature coefficient of a compound formed in

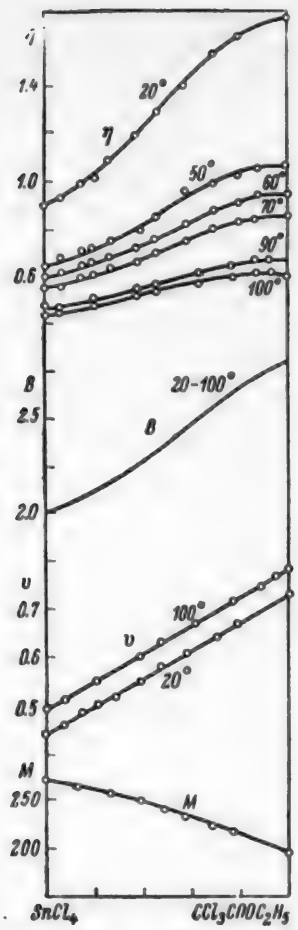

Fig. 1. Property – composition diagram of the $SnCl_4$ – $CCl_3COOC_2H_5$ system.

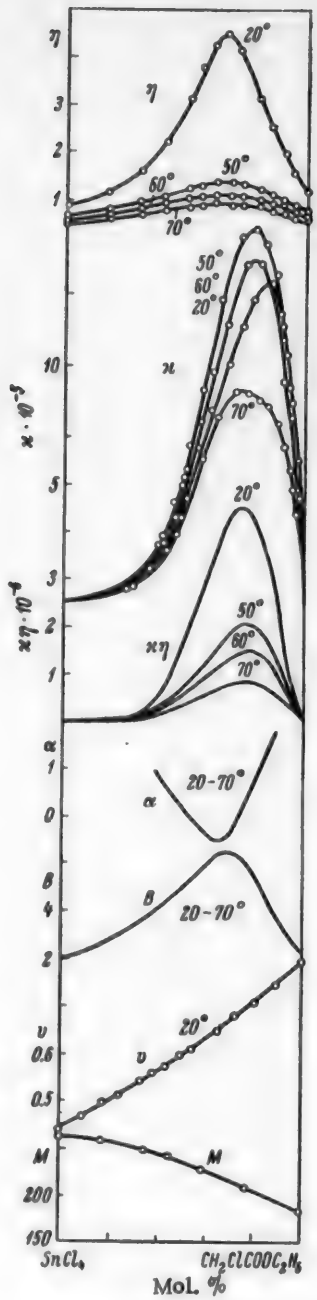

Fig. 2. Property – composition diagram of the $SnCl_4$ – CH_2Cl-$COOC_2H_5$ system.

the system is less than the temperature coefficient of the more viscous component [20]. The curve showing the dependence of B on composition (20 - 100°) appeared as an S-shaped curve, whose form indicated that there was interaction between the components in the system.

The results of cryoscopic measurements, presented in the form of a molecular weight – composition diagram, also indicated the presence of interaction. The dependence of specific volume on composition, expressed in weight percent, gave a straight line at all temperatures and did not reflect interaction.

2. The $SnCl_4$ – $CH_2ClCOOC_2H_5$ system was studied by means of electroconductivity, viscosity and density and also cryoscopically. Mixing stannic chloride with ethyl monochloroacetate was accompanied by considerable heat evolution. Mixtures of stannic chloride with ethyl monochloroacetate had a specific electroconductivity of the order of 10^{-4} Ω^{-1} cm^{-1}. Over a period of time, the electroconductivity of the mixtures decreases slightly.

TABLE 3

$SnCl_4$ (mole %)	Viscosity (in centipoises)				Density (g/cc)			
	20°		60°	70°	20°	50°	60°	70°
0.00	1.19	0.773	0.685	0.612	1.1512	1.1160	1.1051	1.094
4.99	1.51	0.880	0.765	0.661	—	—	—	—
9.98	1.95	1.01	0.847	0.728	1.3006	1.2542	1.2381	1.2204
15.08	2.56	1.13	0.935	0.770	1.3700	1.3205	1.2900	1.2750
19.96	3.20	1.22	0.983	0.823	1.4448	1.3830	1.3632	1.3453
28.53	4.19	1.35	1.06	0.876	1.5643	1.4914	1.4741	1.4501
32.68	4.50	1.37	1.07	0.878	1.6194	1.5443	1.5192	1.5014
38.78	4.24	1.40	1.10	0.905	1.6891	1.6124	1.5892	1.5638
44.11	3.79	1.30	1.07	0.875	1.7446	1.6695	1.6388	1.6214
49.11	3.10	1.28	1.05	0.874	1.7936	1.7060	1.6831	1.6609
59.62	2.20	1.09	0.923	0.780	1.8914	1.8207	1.7946	1.7714
69.50	1.63	0.940	0.825	0.717	1.9779	1.9072	1.8820	1.8584
83.51	1.16	0.789	0.686	0.623	2.0951	2.0240	2.0004	1.9746
100.00	0.888	0.630	0.582	0.539	2.2331	2.1566	2.1313	2.1127

TABLE 4

$SnCl_4$ (mole %)	$x \cdot 10^{-5}$ at 20°	$SnCl_4$ (mole %)	$x \cdot 10^{-5}$ at 50°	$SnCl_4$ (mole %)	$x \cdot 10^{-5}$ at 60°	$SnCl_4$ (mole %)	$x \cdot 10^{-5}$ at 70°
2.90	5.05	2.90	4.97	2.90	4.42	2.90	3.88
5.02	7.45	2.76	5.54	5.13	7.96	4.73	4.79
6.75	9.10	6.54	9.36	7.83	10.4	6.23	5.52
9.19	11.1	9.14	11.7	10.26	12.2	8.51	6.52
12.65	12.8	12.24	13.9	13.96	13.5	11.88	7.55
16.52	13.8	16.01	15.2	18.38	14.4	15.89	8.25
21.15	12.9	20.99	15.8	25.43	14.3	19.74	8.50
25.99	11.7	26.69	15.5	32.24	11.7	23.77	8.85
31.57	10.0	33.69	12.8	38.49	9.78	28.90	8.90
38.84	8.17	42.21	8.89	44.19	7.64	35.75	7.75
45.27	6.59	46.96	6.62	48.80	5.51	42.40	6.04
50.38	5.26	50.88	4.94	53.92	3.49	49.00	4.39
54.25	4.27	58.14	2.80	58.15	2.59	54.09	2.99
61.25	2.51	72.14	0.610	64.83	1.49	58.15	2.30
74.00	0.585	—	—	77.31	0.373	85.66	0.236

TABLE 5

$SnCl_4$ (mole %)	$x\eta \cdot 10^{-6}$				α (in % at 20-70°)	B (in kcal)
	20°	50°	60°	70°		
0	—	—	—	—	—	2.66
10	22.7	12.0	9.90	5.25	1.4	3.96
20	42.4	19.3	14.1	7.09	1.1	5.55
25	45.4	20.2	14.6	8.01	—	—
30	44.7	19.2	13.7	7.92	0.36	6.37
33	—	—	—	—	—	6.45
40	31.7	13.4	9.90	6.29	0.30	6.09
50	16.1	6.63	5.15	3.50	0.60	5.02
60	5.72	2.51	2.09	1.76	—	4.07
70	1.65	0.930	0.830	0.730	—	3.20
80	0.350	0.320	0.220	0.200	—	2.74
90	—	—	—	—	—	2.26
100	—	—	—	—	—	1.98

The results of measuring viscosity, specific conductivity and density are given in Tables 3 and 4; Table 5 gives the results of calculating the corrected electroconductivity, the temperature coefficient of the electroconductivity and also the constant B. Fig. 2 shows property – composition diagrams. As the figure shows, the viscosity isotherms passed through a maximum. With an increase in temperature, the viscosity maximum became flatter. As increasing amounts of ethyl monochloroacetate were added to stannic chloride, the specific electroconductivity increased, at first slowly and then, beginning with 60 mole% of stannic chloride, sharply, reaching a maximum value in the region of stannic chloride concentrations of 15 – 30 mole% (depending on temperature).

Due to the fact that the temperature coefficient changed sign with an increase in temperature, the specific electroconductivity isotherms intertwined with each other irregularly and the position of the maximum on them shifted towards stannic chloride with an increase in temperature. This form of the specific electroconductivity isotherms was produced by the effect of viscosity. When a correction for viscosity was introduced, the electroconductivity fell regularly with an increase in temperature and at all temperatures the maximum on the isotherms occured at 25 mole% of stannic chloride, i.e. at a compound composition of 1 : 3.

The sharp fall in the corrected electroconductivity with an increase in temperature was apparently connected with the fact that the complex compound $SnCl_4 \cdot 3CH_2ClCOOC_2H_5$ was thermally unstable. The curve showing the composition dependence of the temperature coefficient of the electroconductivity passed through a minimum corresponding to 33 – 34 mole% of stannic chloride on the ordinate, i.e. the composition of the compound $SnCl_4 \cdot 2CH_2ClCOOC_2H_5$. The existence of a compound with the composition 1 : 2 was also indicated by the curve showing the composition dependence of the constant B; this curve passed through a maximum lying at 33 – 34 mole% of stannic chloride. The specific volume isotherms showed that there was compression in the system, caused by interaction of the components.

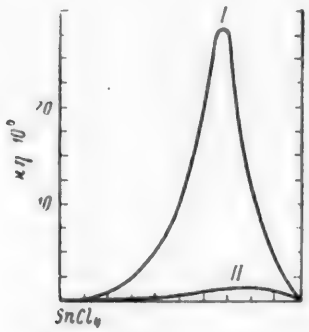

Fig. 3. Corrected electroconductivity of systems. I) $SnCl_4$ – $CH_3COOC_2H_5$, II) $SnCl_4 - CH_2ClCOOC_2H_5$.

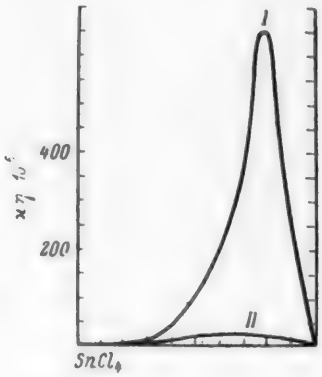

Fig. 4. Corrected electroconductivity of systems. I) $SnCl_4 - CH_3COOH$, II) $SnCl_4 - CH_3COOC_2H_5$.

Cryoscopic measurements of the molecular weight of the system also indicated interaction of the components. Thus, on the basis of the results of measuring the viscosity, electroconductivity and density, we came to the conclusion that with ethyl monochloroacetate, stannic chloride formed the two compounds $SnCl_4 \cdot 2CH_2ClCOOC_2H_5$ and $SnCl_4 \cdot 3CH_2ClCOOC_2H_5$.

DISCUSSION OF RESULTS

A study of the behavior of stannic chloride with the esters ethyl trichloroacetate and ethyl monochloroacetate gave the following results. The presence of interaction in the $SnCl_4 - CCl_3COOC_2H_5$ system was established. Solutions of stannic chloride in ethyl trichloroacetate did not conduct an electric current; consequently, salt forming products were not produced in the interaction of the components. Since ethyl trichloroacetate has sharply expressed acidic properties, its molecules did not act as a base with respect to $SnCl_4 \cdot 2CCl_3COOC_2H_5$; therefore, the acid-base interaction apparently stopped with the formation of a complex compound in the ratio

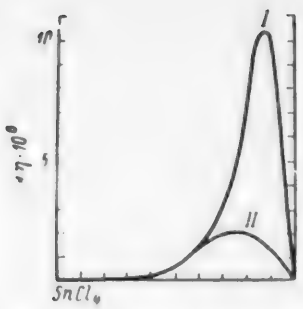

Fig. 5. Corrected electroconductivity of systems. I) $SnCl_4$ - $CH_2ClCOOH$, II) $SnCl_4 - CH_2ClCOOC_2H_5$.

1 : 2. A study of the $SnCl_4 - CCl_3COOH$ system established that stannic chloride did not interact with trichloroacetic acid [21]. Consequently, replacement of the hydrogen of the carboxyl group by C_2H_5 considerably increased the basic properties of the molecule, as a result of which, ethyl trichloroacetate underwent an acid-base interaction with stannic chloride.

A study of the $SnCl_4 - CH_2ClCOOC_2H_5$ system by physico-chemical analysis methods showed that the components of the system underwent acid-base interaction with the formation of the compounds $SnCl_4 \cdot 2CH_2ClCOOC_2H_5$ and $SnCl_4 \cdot 3CH_2ClCOOC_2H_5$. The presence of electroconductivity in the system and the existence of the compound $SnCl_4 \cdot 3CH_2ClCOOC_2H_5$ indicated that the interaction proceeded further than in the $SnCl_4 - CCl_3COOC_2H_5$ system and showed that ethyl monochloroacetate has more strongly expressed basic properties than ethyl trichloroacetate. In our opinion, the compound $SnCl_4 \cdot 2CH_2ClCOOC_2H_5$ is a complex acid, capable of donating the cation $C_2H_5^+$ to a base; in our case, the base which adds this cation is an ethyl monochloroacetate molecule. As a result of such an acid-base interaction, the salt $[SnCl_4(CH_2ClCOO)_2]C_2H_5^- \cdot CH_2ClCOO(C_2H_5)_2^+$ is formed and this also causes the electroconductivity of the system.

According to the data of Moshchen [4], the $SnCl_4 - CH_3COOC_2H_5$ system has a considerable electroconductivity. The specific electroconductivity isotherms pass through two maxima and a minimum, whose position on the diagram corresponds to 33 mole% of stannic chloride, i.e. the composition of the compound $SnCl_4 \cdot 2CH_3COOC_2H_5$. In Fig. 3 we compare the isotherms of the corrected electroconductivity of the $SnCl_4 - CH_3COOC_2H_5$ and $SnCl_4 - CH_2ClCOOC_2H_5$ systems. The figure shows that the value of the corrected electroconductivity of solutions formed by ethyl acetate is considerably higher than that of solutions of ethyl monochloroacetate. Previously, one of us [22, 23] showed that the value of the corrected electroconductivity was a measure of the extent of acid-base interaction: the greater the interaction, the greater was the corrected electroconductivity. From this it follows that in the $SnCl_4 - CH_3COOC_2H_5$ system the interaction is greater than in the $SnCl_4 - CH_2ClCOOC_2H_5$ system. In comparison with monochloroacetic acid, ethyl monochloroacetate also has more basic properties. Monochloroacetic acid [24] interacts with stannic chloride and forms conducting solutions with it. Fig. 4 shows a comparison of the values of the corrected electroconductivity of the $SnCl_4 - CH_3COOH$ [7] and $SnCl_4 - CH_3COOC_2H_5$ [4] systems. Fig. 5 shows the same data for the $SnCl_4 - CH_2ClCOOH$ and $SnCl_4 - CH_2ClCOOC_2H_5$ systems. The figures show that the isotherms of the corrected electroconductivity of the systems formed by CH_3COOH and $CH_2ClCOOH$ are considerably higher on the diagram than the isotherm belonging to the system formed by their esters. Since their esters have more strongly expressed basic properties, the opposite state of affairs was to be expected at first sight. However, taking into account the fact that the electroconductivity arises as a result of secondary acid-base interaction between the complex acids ($SnCl_4 \cdot 2RCOOH$ and $SnCl_4 \cdot 2RCOOR'$) and oxonium bases (RCOOH and RCOOR'), we can explain the fall in the corrected electroconductivity in going from RCOOH to RCOOR' by the fact that in this case the corrected electroconductivity characterizes the strength of the complex acids and not the strength of the oxonium bases.

Thus, Figs. 4 and 5 clearly show that the complex acids $SnCl_4 \cdot 2RCOOH$ are stronger acids than $SnCl_4 \cdot 2RCOOR'$. Comparison of the behavior of ethyl acetate and ethyl monochloroacetate with respect to stannic chloride shows that the electroconductivity in the systems formed by stannic chloride and esters arises under conditions when the compound $SnCl_4 \cdot 3RCOOR'$ is formed in solution.

SUMMARY

1. By physico-chemical analysis methods (conductimetry, viscosimetry, volumetry and cryoscopy) a study was made of the $SnCl_4 - CCl_3COOC_2H_5$ and $SnCl_4 - CH_2ClCOOC_2H_5$ systems.

2. It was established that in the $SnCl_4 - CCl_3COOC_2H_5$ system, there was interaction between the components, which apparently stopped at the stage of the formation of the compound $SnCl_4 \cdot 2CCl_3COOC_2H_5$.

Electroconductivity was practically absent from this system. In the $SnCl_4 - CH_2ClCOOC_2H_5$ system interaction between the components proceeded further with the formation of the compounds $SnCl_4 \cdot 2CH_2ClCOOC_2H_5$ and $SnCl_4 \cdot 3CH_2ClCOOC_2H_5$. The formation of the compound $SnCl_4 \cdot 3CH_2ClCOOC_2H_5$ caused the electroconductivity of the system.

3. Electroconductivity in systems formed by stannic chloride with esters arises when compounds of the type $SnCl_4 \cdot 3RCOOR$ are formed.

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INTERACTION OF STANNIC CHLORIDE WITH ESTERS. II

T. Sumarokova, R. Omarova and N. Kuz'menko

Institute of Chemical Sciences, Academy of Sciences, Kazakh, SSR

Esters of monocarboxylic acids interact [1 – 9] with stannic chloride with the formation of the compounds $SnCl_4 \cdot 2RCOOR'$ and $SnCl_4 \cdot 3RCOOR'$. The electroconductivity of the $SnCl_4$ – RCOOR' system is caused by the formation of the compound $SnCl_4 \cdot 3RCOOR'$ [7].

In the present work we were interested in the effect of the length of the aliphatic alcohol radical on the acid-base properties of esters. According to Kendall [10, 11], the basic properties increase with an increase in the length of the radical. The truth of this proposal of esters was demonstrated by a study of their interaction with carboxylic acids [12 – 15]. To determine whether these differences appeared in relation to stannic chloride (aprotonic acid), we undertook a study of the $SnCl_4 - CH_3COOC_8H_{17}$ and $SnCl_4 - CH_3COOC_{16}H_{33}$ systems by means of the viscosity, density and electroconductivity.

EXPERIMENTAL

Cetyl acetate and octyl acetate were synthesized from previously dried and purified alcohols, and glacial acid. Octyl acetate was first dried over baked sodium sulfate and them distilled many times. A fraction with b.p. 185° at 692 mm was collected for the work. Cetyl acetate (dried with baked sodium sulfate) was vacuum distilled twice; a fraction with b.p. 174 – 176° at 12 mm was collected and fractionated by freezing. The cetyl acetate had m.p. 24°.

1. The $SnCl_4 - CH_3COOC_8H_{17}$ system was studied by means of the electroconductivity, viscosity and density at 25 and 50°. The results of measuring the properties and also the calculated temperature coefficient of electroconductivity, corrected electroconductivity and constant B are presented in Table 1. Fig. 1 shows property – composition diagrams. The figure shows that the viscosity isotherms pass through a sharply expressed maximum, occurring at 33 mole% of stannic chloride; the position of the maximum indicates the formation of the compound $SnCl_4 \cdot 2CH_3COOC_8H_{17}$.

The specific conductivity isotherms pass through a maximum and have an inflection point. With an increase in temperature, the specific electroconductivity maximum is displaced towards octyl acetate and the point of inflection, occurring at 33 mole% of stannic chloride, has a tendency to disappear. The isotherms of the corrected electroconductivity pass through a maximum, corresponding to 33 mole% of stannic chloride. With an increase in temperature, the value of the corrected electroconductivity falls sharply, which is apparently connected with the thermal instability of the compound formed. The curve of the electroconductivity temperature coefficient also passes through a maximum at 33 mole% of stannic chloride, i.e., at the composition of the compound $SnCl_4 \cdot 2CH_3COOC_8H_{17}$. Unfortunately we could not trace the position of the maximum more accurately on the curves of the electroconductivity temperature coefficient and the corrected electroconductivity since we had a very small amount of octyl acetate available; therefore, the specific electroconductivity was measured for only five mixtures. However, the analogy with the course of the curves obtained for the following system convinced us of the accuracy of the results and their interpretation.

The curve showing the composition dependence of the constant B passes through a maximum corresponding to 33 mole% of stannic chloride. The dependence of the specific volume on the composition, expressed in weight percents, shows that there is compression in the system produced by reaction of the components. Thus, on the

TABLE 1

$SnCl_4$ (mole %)	Viscosity (in centipoises)		$\varkappa \cdot 10^{-5}$		Density (g/cc)		$x\eta \cdot 10^{-6}$		α (in %)	B (in kcal)
	25°	50°	25°	50°	25°	50°	25°	50°	25—50°	
100.00	—	0.639	—	—	—	2.1566	—	—	—	1.98
89.57	1.62	0.959	—	—	1.9295	1.8751	—	—	—	4.24
76.75	4.57	2.47	1.3	1.9	—	—	0.59	0.47	1.8	4.71
58.26	8.12	3.79	1.5	2.5	1.5051	1.4720	1.2	0.95	2.7	5.83
50.76	16.4	6.36	1.3	3.0	1.3885	1.3577	2.1	1.9	5.2	7.25
33.90	65.1	13.6	0.77	—	1.2095	1.1791	5.0	3.3	8.8	12.0
20.32	12.4	5.08	0.72	1.8	1.0318	1.0101	0.91	0.91	6.0	6.83
0.00	1.67	1.05	—	—	0.8179	0.7991	—	—	—	3.55

TABLE 2

$SnCl_4$ (mole %)	Viscosity (in centipoises)				Density (in g/cc)			
	40°	50°	60°	70°	40°	50°	60°	70°
0.00	5.01	3.85	3.20	2.67	0.8455	0.8379	0.8310	0.8238
12.24	10.4	7.57	5.63	4.30	—	—	—	—
26.08	31.0	18.6	11.6	7.79	1.0304	1.0220	1.0112	1.0013
33.27	43.8	24.8	15.2	9.63	1.0926	1.0824	1.0715	1.0600
38.66	37.9	22.9	14.3	9.46	1.1365	1.1268	1.1156	1.1043
54.13	15.4	11.0	8.15	6.21	1.2754	1.2648	1.2548	1.2429
70.94	5.46	4.36	3.60	3.02	1.4909	1.4748	1.4618	1.4506
84.97	2.22	1.90	1.65	1.44	1.7560	1.7422	1.7233	1.7062
100.00	0.699	0.630	0.582	0.539	2.1678	2.1566	2.1313	2.1127

TABLE 3

$SnCl_4$ (mole %)	$\varkappa \cdot 10^{-6}$			
	40°	50°	60°	70°
12.24	2.25	2.60	3.00	3.30
26.08	4.35	5.30	6.55	7.95
33.00	4.50	6.00	7.40	8.80
38.66	4.80	6.30	7.80	9.30
45.09	5.80	6.95	8.10	9.30
54.13	5.70	6.40	7.20	8.00
70.94	3.30	4.00	4.80	5.50
84.97	1.20	1.60	1.90	2.30

basis of data from physicochemical analysis of the $SnCl_4 - CH_3COOC_8H_{17}$ system, we arrive at the conclusion that the components of the system react with the formation of the complex compound $SnCl_4 \cdot 2CH_3COOC_8H_{17}$.

2. $SnCl_4 - CH_3COOC_{16}H_{33}$ system. When stannic chloride was mixed with cetyl acetate, a colorless crystalline compound was formed and a considerable amount of heat was evolved. Mixtures of stannic chloride and cetyl acetate conducted an electric current. The $SnCl_4 - CH_3COOC_{16}H_{33}$ system was studied by means of the electroconductivity, viscosity and density at 40, 50, 60 and 70°. The results of the measurements are given in Tables 2 and 3; Table 4 shows the results of calculating the corrected electroconductivity, the electroconductivity temperature coefficient and the constant B.

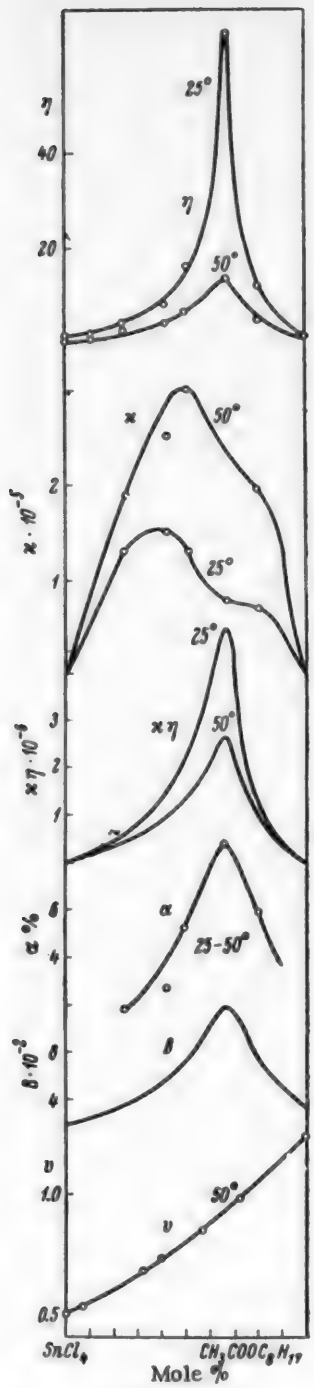

Fig. 1. Property – composition diagrams of the $SnCl_4 - CH_3COOC_8H_{17}$ system.

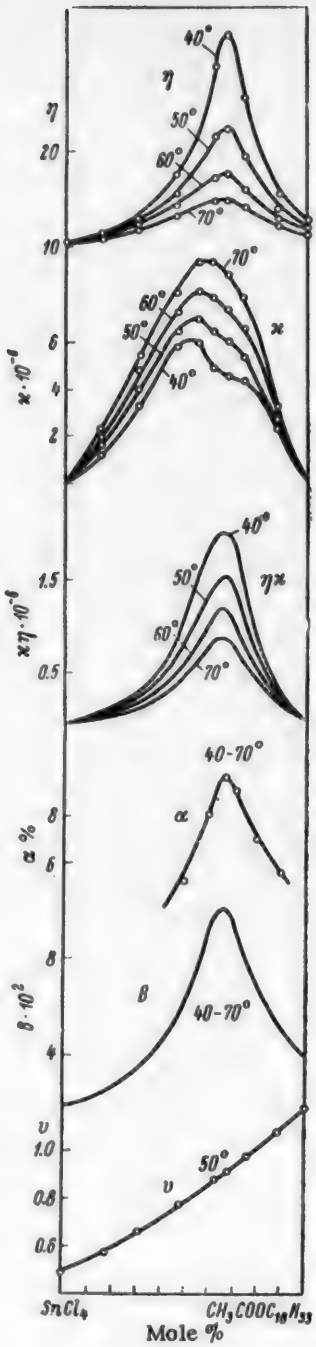

Fig. 2. Property – composition diagrams of the $SnCl_4 - CH_3COOC_{18}H_{33}$ system.

TABLE 4

$SnCl_4$ (mole %)	$x\eta \cdot 10^{-6}$				α (in %) 70–40°	B (in kcal)
	40°	50°	60°	70°		
0	—	—	—	—	—	4.06
10	0.193	0.159	0.135	0.125	5.7	5.93
20	0.768	0.579	0.461	0.408	7.0	9.02
30	1.89	1.44	1.06	0.817	9.1	10.5
33	1.97	1.49	1.13	0.845	9.6	10.5
40	1.83	1.40	1.10	0.842	8.1	8.85
50	1.10	0.898	0.762	0.613	5.2	6.60
60	0.525	0.462	0.419	0.365	4.6	5.14
70	0.199	0.197	0.196	0.178	—	4.02
80	0.062	0.064	0.064	0.058	—	3.17
90	0.011	0.013	0.009	0.009	—	2.45
100	—	—	—	—	—	1.98

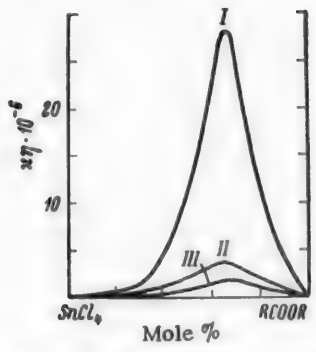

Fig. 3. Corrected electroconductivity of systems. I) $SnCl_4 - CH_3COOC_2H_5$, II) $SnCl_4 - CH_3COOC_8H_{17}$, III) $SnCl_4 - CH_3COOC_{16}H_{33}$.

Fig. 2 shows property – composition diagrams of the $SnCl_4 - CH_3COOC_{16}H_{33}$ system. The viscosity isotherms pass through a sharply expressed maximum. With an increase in temperature, the maximum is shifted towards stannic chloride. The maximum on the viscosity isotherms indicates the formation of the complex compound $SnCl_4 \cdot 2CH_3COOC_{16}H_{33}$.

The specific electroconductivity increases sharply as cetyl acetate is added to stannic chloride, passes through a maximal value and then falls. At a point corresponding to 33 mole% of stannic chloride, the specific electroconductivity isotherms show inflection, which is sharply expressed on the isotherm at 40°.

With an increase in temperature the inflection become less sharp and disappears completely at 70°, while the maximum on the specific electroconductivity isotherms is shifted towards cetyl acetate. When a correction for viscosity is introduced, the electroconductivity passes through a maximum value at 33 – 34 mole% of stannic chloride. The curve expressing the composition dependence of the temperature coefficient of electroconductivity passes through a maximum at 33 mole% of stannic chloride. Fig. 2 shows that the maximum change in the constant B occurs at the composition of the compound $SnCl_4 \cdot 2CH_3COOC_{16}H_{33}$.

The curve of the change in specific volume with composition, expressed in weight percents, shows that when stannic chloride is mixed with cetyl acetate there is compression, caused by interaction of the components.

Thus, on the basis of data from physicochemical analysis of the system, we arrive at the conclusion that the complex compound $SnCl_4 \cdot 2CH_3COOC_{16}H_{33}$ is formed in the sytem. The compound was isolated in the free state and had m.p. 56°. The presence of electroconductivity in the system indicates the existence of the compound $SnCl_4 \cdot 3CH_3COOC_{16}H_{33}$.

DISCUSSION OF RESULTS

A study of electroconductivity, viscosity and density of the $SnCl_4 - CH_3COOC_8H_{17}$ system showed that the components of the system formed the compound $SnCl_4 \cdot 2CH_3COOC_8H_{17}$. The existence of this compound was indicated by the maximum in the viscosity, temperature coefficient of electroconductivity and constant B. We arrived at the conclusion that the compound $SnCl_4 \cdot 3CH_3COOC_8H_{17}$ existed on the basis of the presence of electroconductivity in the system, since from theoretical considerations and also experimental data, we previously [7] showed that the appearance of electroconductivity in analogous systems was connected with the formation of compounds of the type $SnCl_4 \cdot 3A$ and $SnCl_4 \cdot 4A$.

A similar picture was obtained in the $SnCl_4 - CH_3COOC_{16}H_{33}$ system. Like the previous one, this system conducted an electrical current. The viscosity isotherms passed through a sharply expressed maximum at the composition of the compound with a ratio of 1 : 2. The presence of electroconductivity in the solutions showed that the system formed an interaction product of a salt-like character. In our opinion, this product is the complex compound $SnCl_4 \cdot 3CH_3COOC_{16}H_{33}$, although we did not obtain direct indications of the existence of a compound with a 1 : 3 composition.

In Fig. 3, we compare the values of the corrected electroconductivity at 50° of the systems $SnCl_4 - CH_3COOC_2H_5$ [4], $SnCl_4 - CH_3COOC_8H_{17}$ and $SnCl_4 - CH_3COOC_{16}H_{33}$. Fig. 3 shows that value of the corrected electroconductivity of solutions formed by cetyl acetate is considerably less than that of solutions of octyl acetate and particularly ethyl acetate. The picture obtained is explained by the fact that the formation of the complex compounds $SnCl_4 \cdot 3RCOOR'$ is a secondary acid-base reaction, proceeding through the stage of the formation of the complex acids $SnCl_4 \cdot 2RCOOR'$, whose strength decreases with an increase in the length of the radical. A similar rule was established by a study of the systems formed by stannic chloride with carboxylic acids [16, 17].

SUMMARY

1. By physico-chemical analysis methods a study was made of the interaction of stannic chloride with octyl acetate and cetyl acetate. The existence of the compounds $SnCl_4 \cdot 2CH_3COOC_8H_{17}$ and $SnCl_4 \cdot 2CH_3COOC_{16}H_{33}$ was established and a hypothesis was put forward on the existence of the compounds $SnCl_4 \cdot 3CH_3COOC_8H_{17}$ and $SnCl_4 \cdot 3CH_3COOC_{16}H_{33}$.

2. It was shown that the strength of the complex acids $SnCl_4 \cdot 2RCOOR'$ falls as the length of the alcohol radical increases.

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EXPERIMENTAL ERRORS IN CERTAIN WORK ON THE STUDY OF TETRACHLORIDES OF GROUP IV ELEMENTS

Yu. Ya. Fialkov

Kiev Polytechnical Institute

Much work has been devoted to the chemistry of tetrachlorides of group IV elements. In particular this refers to tin and titanium tetrachlorides, which have been the subject of a whole series of investigations due to their very well expressed capacity for complex formation.

The most characteristic property of tetrachlorides of group IV elements is an extremely great tendency for hydrolysis. Therefore, in work with them the greatest attention must be paid to careful drying of all substances used for the work and guaranteeing conditons excluding the entrance of moisture into the reaction vessels. The presence of even insignificant amounts of hydroxides of these elements and also hydrogen chloride alters the physical and physicochemical properties of the solutions and the compounds formed so much that the slightest neglect of this condition may lead and has led in a series of cases to inaccurate experimental results and even to completely incorrect conclusions.

In the present communication, we wish to point out certain work on the study of tetrachlorides of group IV elements, where due to a careless experiment, incorrect conclusions have been drawn.

In the work of Yu. N. Vol'nov [1], it was stated that when silicon tetrachloride was mixed with ethyl acetate, heat evolution was observed; the mixtures acquired a straw yellow color. From this the author concluded that silicon tetrachloride and ethyl acetate reacted with each other at room temperature. Vol'nov arrived at the same conclusion as regards isoamyl acetate: when silicon tetrachloride was mixed with the ester, he observed slight heat evolution and the formation of a "meat-red" solution; the mixtures acquired an opalescence.

In studying systems of silicon tetrachloride and esters by means of viscosity and dielectric constant (in particular, the silicon tetrachloride – ethyl acetate system), together with V. V. Udovenko, we [2, 3] showed that at normal temperatures silicon tetrachloride does not interact with esters. However, in no case did we observe heat evolution or the appearance of any color on mixing the components. Apparently, Vol'nov worked with insufficiently purified and dried esters. The latter state of affairs in particular is indicated by the fact that when he mixed silicon tetrachloride with isoamyl acetate, he observed opalescence (the formation of silicic acid).

Then in the same work Vol'nov states that by distillation of mixtures of silicon tetrachloride with p-cresyl acetate he obtained several fractions, which, on being poured into water, yielded this ester and 4 moles of hydrogen chloride to 1 mole of silicic acid. From this Vol'nov concluded that with p-cresyl acetate, silicon tetrachloride formed molecular compounds, which were isolated by distillation. Actually, Vol'nov did not investigate the ratio of silicon tetrachloride to ester in the fractions he isolated.

The existence of the compounds proposed by Vol'nov seemed very improbable to us. As already noted, silicon tetrachloride is incapable of forming addition products with oxygen-containing organic compounds in general and with esters in particular, even at low temperatures. The existence of such products at distillation temperatures seemed even more surprising.

Starting from these considerations, we repeated the experiment described in Vol'nov's article. By distillation of a mixture of silicon tetrachloride and p-cresyl acetate with a large fractionating column, we obtained

two fractions: one distilling in the range 54 – 60° and the second in the range 208 – 212°. Investigations showed that the first fraction was pure silicon tetrachloride and the second, the pure original ester. Thus, the conclusion drawn by Vol'nov [1] was not confirmed*.

A similar experiment, which we carried out with m-cresyl acetate led to the same results.

The addition products of acetoacetic esters and tetrachlorides of group IV elements are described in article [4]. According to this communication, tin and titanium tetrachlorides give compounds with a 1 : 1 composition and silicon tetrachloride adds two molecules of acetoacetic ester. The authors of this article reported that the latter compound was obtained in the form of straw-yellow crystals by mixing together 10 g of ester and 5 g of $SiCl_4$, first cooled with solid carbon dioxide. The substance was extremely unstable and decomposed even at 0° with the evolution of hydrogen chloride.

Data in the work cited raise a series of questions.

Firstly, why does the behavior of silicon tetrachloride towards acetoacetic ester differ so sharply from its behavior towards other oxygen-containing organic substances, since this compound (see [4]) is the sole example of a molecular compound with oxygen-containing substances? In the work of Udavenko and the author of the present article [2, 3], by physico-chemical analysis methods it was shown that silicon tetrachloride did not show the slightest tendency towards the formation of molecular compounds either with esters or with ketones.

Secondly, there is an objection to the method of determining chlorine: a sample of the compound was dissolved in water and then the hydrochloric acid formed was titrated with 0.1 N sodium hydroxide solution. However, a "blank" experiment showed that if potassium hydroxide was added to an aqueous solution of acetoacetic ester, a phenolphthalein color only appeared after quite a considerable amount of alkali had been added to the acetoacetic ester. It is all the more incomprehensible why analysis of the compound obtained by this method gave almost the theoretical amount of chlorine calculated for a 1 : 2 compound.

Thirdly, it is incomprehensible why the coordination number of silicon in this case is greater than the coordination numbers of tin and titanium, since tetrachlorides of the latter give compounds with a 1 : 1 composition. Meanwhile, on the basis of the great inertness of silicon tetrachloride in complex formation, one would expect the reverse relation in the best case.

We repeated the experiment on the preparation of a compound of silicon tetrachloride and acetoacetic ester, described in [4], and when the carbon dioxide-cooled components were poured together, we did not observe the precipitation of crystals. At low temperatures (of the order of -35°), the mixture separated into layers; we observed no evolution of hydrogen chloride from mixtures of acetoacetic ester and silicon tetrachloride, even at + 18°.

We made many attempts to prepare compounds of silicon tetrachloride and acetoacetic ester, but they were always unsuccessful. Thus, the data in [4] on the compound with S_4Cl_4 must be considered unconfirmable.

In 1952 Trost published a paper [5], in which he briefly reported the results of studying the interaction of silicon tetrachloride with a series of oxygen-containing organic substances. Trost stated that "organic molecules, containing oxygen, . . . add to silicon tetrachloride. If silicon tetrachloride is mixed at low temperatures with alcohols, ketones, acids or esters, yellow solutions are formed. On heating to room temperature, the yellow color does not change, provided that the silicon tetrachloride is not present in excess and that the solutions do not contain alcohol. If the organic component is present in excess (about 80 vol. %), then at room temperature the solutions solidify and are converted into a clear, homogeneous, friable solid mass. This solid substance frequently shrivels, evolving liquid". This phenomenon occurs in the case of ethyl acetate, amyl acetate, butyric and caproic acids, the aldehydes corresponding to these acids, acetone, cyclopentanone, mesityl oxide, dibutyl ether, anisole and a series of alcohols. It was then stated that these compounds formed more readily if the solutions of silicon tetrachloride in the organic component were cooled strongly: on raising the temperature, the frozen mixture changed into such solid substances. Trost considers that in all these cases, molecular compounds of silicon tetrachloride are formed.

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* Incidentally, it is incomprehensible why the author of this work reported that the ester he used for this work had b.p. 110 – 112°, which is possibly a misprint (it should be 210 – 212°).

The results reported by Trost disagree so much with known facts on the behavior of silicon tetrachloride towards oxygen-containing organic substances that we are inclined to think that the conclusions he arrived at are the results of some sort of misunderstanding. Trost recommends strong cooling of the mixtures with their subsequent heating to room temperature as conditions for the formation of "solid products". Despite the fact that the uselessness of such an operation was evident, we repeated Trost's experiments by cooling solutions of silicon tetrachloride in a series of oxygen-containing organic substances, from those listed above, to liquid air temperature. This did not lead to the formation of any compounds. We stored the sealed ampoules with these solutions for more than two years and during this time there was no change in color or in the physical state. Silicon tetrachloride reacted with alcohols and acetone at room temperature to form the corresponding silico-organic compounds, as should occur in accordance with reactions studied a long time ago [6], and quite independently of whether the mixtures and their components were first cooled strongly or not.

We should also note that Trost described neither the working procedure, the analysis of the "compounds" he obtained nor the nature of the liquids, evolved during "shriveling" of the solid products. Apparently, the organic preparations he used for the work were considerably contaiminated with water and the "compounds" obtained were nothing more than silicic acid gel.

The last of the works which we wish to consider is that of Wertiporoch and Altman [7]. It contains data on the electroconductivity of silicon, tin and titanium tetrachloride solutions in various organic solvents. In all cases they observed conductivity, which the authors ascribed to the formation of addition products of the tetrachlorides to organic substances.

The first type of solvents used by the authors were alcohols. The very fact that solutions of silicon and titanium tetrachloride in alcohols were obtained is surprising, since it is known that these tetrachlorides react with alcohols with the liberation of hydrogen chloride. Hence we are lead to assume that in the case of solutions of silicon and titanium tetrachlorides in alcohols, the electroconductivity is caused not by the formation of addition products, but by solvolysis. In other words, the conductivity should be considered as due to hydrogen chloride. An examination of the numerical data presented by Wertiporoch and Altman supports this conclusion. While the electroconductivity of solutions of silicon and titanium tetrachlorides in methyl alcohol (at a tetrachloride concentration of 2.5 mole%) is of the order of 10^{-2} Ω^{-1} cm^{-1}, the electroconductivity of a solution of stannic chloride of the same concentration is two orders less. Were the electroconductivity caused by complex formation, the solutions of silicon tetrachloride, as the weakest complex-former, should conduct worst of all and solutions of stannic chloride should conduct best of all. Incidentally, compounds of the latter tetrachloride with alcohols have been identified [8] and it has been shown that solvolysis of the chloride does not occur when it is dissolved in alcohols. Thus, the conductivity of alcohol solutions of stannic chloride may actually be considered as due to complex formation. If we consider that the conductivity is caused by the evolution of hydrogen chloride, then it is evident that the greatest electroconductivity must be in solutions of silicon and titanium tetrachloride, as actually observed.

The authors of the paper discussed [7] did not report whether, on solution of silicon and titanium tetrachlorides in alcohols, they observed the formation of any precipitates or esters and chloroesters of the corresponding orthoacids. However, at the very low concentrations at which they worked the solvolysis products formed could have dissolved completely in the excess solvent, not to speak of hydrogen chloride, which is very readily soluble in alcohols.

Similar results were obtained by Wertiporoch and Altman in studying solutions of tetrachlorides in esters, aldehydes and nitriles.

We investigated the conductivity of solutions of silicon tetrachloride in methyl and ethyl acetates, anisole, dimethyl sulfide, benzophenone and nitrobenzene and did not find conductivity in a single case.

Data on the presence of conductivity in solvents, where solvolysis is excluded, presented in [7], was in all probability caused by insufficient protection of the solutions from contact with moisture. Actually, in the work it is possible to find indirect indications that moisture was present in the solvents used. Thus, for example, it was reported that on solution of silicon tetrachloride in benzaldehyde, turbidity and the evolution of hydrogen chloride was observed. Meanwhile, experiment shows that when carefully dried benzaldehyde is mixed with silicon tetrachloride such phenomena are not observed and the solution remains clear.

SUMMARY

It was shown that all the information in the papers [1, 4, 5 and 7] on molecular compounds of silicon tetrachloride is incorrect. In most cases the source of the error was insufficient care in the protection of the solutions of tetrachlorides from contact with moisture.

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ALKYLATION OF p-DIISOPROPYLBENZENE WITH PROPYLENE IN THE PRESENCE OF A $BF_3 \cdot H_3PO_4$ CATALYST

S. V. Zavgorodnii and R. N. Volkov

Voronezh State University

In the present work a study was made of the alkylation of p-diisopropylbenzene with propylene in the presence of a $BF_3 \cdot H_3PO_4$ catalyst in the temperature range from 3 to 105° and ratios of p-diisopropylbenzene to propylene to catalyst of 1 – 5 : 1 : 0.1 – 0.5. It was found that the alkylation yielded triisopropylbenzenes and tetraisopropylbenzenes. The triisopropylbenzenes were a mixture of 1, 2, 4- and 1, 3, 5-triisopropylbenzenes. The relative content of these in the mixture was 80 – 82 and 18 – 20%, respectively; depending on the conditions, the total yield was 53 – 84% of theoretical. 1, 2, 4, 5-Tetraisopropylbenzene was obtained in a yield of 5 – 29% of theoretical.

The best alkylation conditions were molar ratios of p-diisopropylbenzene to propylene to catalyst of 3 : : 1 : 0.3, a temperature of 60°, a propylene input rate of 1.5 liter/hour and additional stirring of the reaction mixture (after introduction of the calculated amount of propylene) for 40 minutes. Under these conditions, the triisopropylbenzenes were obtained in 81% yield and 1, 2, 4, 5-tetraisopropylbenzene in 15% yield. In this case, hardly any other products were formed. Increasing the rate of propylene input to 2.4 liters/hour slightly lowered the yield of tri- and tetraisopropylbenzenes. Lowering the reaction temperature to 20 and 40° decreased the yield of triisopropylbenzenes to 53 and 74%, respectively, and of tetraisopropylbenzene to 5 and 9%. At 2 – 5° the reaction proceeded very slowly. The yield of triisopropylbenzenes was 18% and of tetraisopropylbenzene, about 1%. Raising the temperature to 80° did not have a noticeable effect on the yield of the main products. At 105° cleavage of the molecular compound $BF_3 \cdot H_3PO_4$ was observed, the conversion of propylene decreased noticeably and the yields of triisopropylbenzenes and tetraisopropylbenzene fell. Decreasing the relative amounts of p-isopropylbenzene to 2 and less moles per mole of propylene considerably lowered the yield of triisopropylbenzenes and raised the yield of tetraisopropylbenzene and the amount of residue. The amount of catalyst had a considerable effect on the yield of alkylation products as is shown by data in the table.

EXPERIMENTAL

The p-diisopropylbenzene had b.p. 209 – 210°, d_4^{20} 0.8583 and n_D^{20} 1.4896. It was isolated from the polyisopropylbenzene residues, formed in the synthesis of cumene from benzene and propylene in the presence of a $BF_3 \cdot H_3PO_4$ catalyst. A fraction of polyisopropylbenzenes with b.p. 90 – 93° (13 mm) was treated with oleum and then with concentrated sulfuric acid until the acid layer had a pale yellow color and the hydrocarbon layer was passed through "Kil" clay, washed with water, alkali and again with water, dried and distilled.

The propylene used was a propane-propylene fraction containing 80% of propylene, 6% of ethylene and 1% of isobutylene.

The alkylation was carried out by the usual method: dry propylene was passed at a rate of 1.5 – 2.5 liters per hour into a three-necked flask, fitted with a stirrer, a thermometer and a gas inlet tube. The induction period varied from 10 to 30 minutes, depending on the temperature and the amount of catalyst. The color of the complex changed from pale yellow at the beginning of the reaction to yellow at the end. When the given amounts of propylene had been introduced into the reactor, the mixture was then stirred for a further definite time at the experimental temperature, introduced into a separatory funnel and the lower, catalyst layer separated and then

Alkylation of p-Diisopropylbenzene With Propylene

Molar ratios of p-diisopropylbenzene to propylene to $BF_3 \cdot H_3PO_4$	Temperature	Propylene input rate (liters/hr)	Time of stirring (in hours)	Yield (%)		Residue (in g)
				triisopropylbenzenes	tetraisopropylbenzene	
3 : 1 : 0.5	60°	2.4	4	73.1	9.1	5.3
3 : 1 : 0.4	60	2.4	4	77.1	8.6	4.0
3 : 1 : 0.3	60	2.4	4	78.8	9.6	2.0
3 : 1 : 0.2	60	2.0	4	76.5	9.0	3.0
3 : 1 : 0.15	60	0.8	8	71.0	6.8	2.5
3 : 1 : 0.1	60	2.0	4	60.2	6.0	1.6
3 : 1 : 0.3	3	2.0	3	17.8	0.8	6.0
3 : 1 : 0.3	20	2.4	4	52.8	4.9	2.0
3 : 1 : 0.3	40	2.4	4	74.0	9.4	3.2
3 : 1 : 0.3	80	2.4	4	79.2	8.9	3.0
3 : 1 : 0.3	95	2.4	4	75.4	8.4	4.5
3 : 1 : 0.3	105	2.4	2	62.3	6.1	4.6
5 : 1 : 0.5	60	1.8	3	84.2	8.7	1.8
3 : 1 : 0.3	60	2.7	0.5	73.6	13.3	7.7
3 : 1 : 0.3	60	1.5	0.7	81.3	15.1	1.6
2 : 1 : 0.2	60	2.2	4	65.4	13.8	5.1
1.5 : 1 : 0.15	60	2.4	5	56.8	15.1	8.2
1 : 1 : 0.1	60	2.2	6	47.5	16.8	16.0
0.7 : 1 : 0.07	65	2.2	6	49.4	28.9	20.0

Note: We used 246 – 248 g of p-diisopropylbenzene for each experiment. The reaction temperature deviated from that given over a range of ± 2°.

returned to the upper hydrocarbon layer after decomposition with water. The products were washed with water, neutralized with sodium carbonate or sodium hydroxide solution, dried with calcium chloride and distilled from a Favorskii flask with a fractionating head 50 cm long or on a fractionating column with an efficiency of 25 – 30 theoretical plates. In the isolation of tetraisopropylbenzene, fractionation was combined with freezing out. The uncrystallizable residue, boiling in the range 140 – 200° at 5 mm did not contain unsaturated hydrocarbons and had n_D^{20} 1.550 – 1.560; when oxidized with nitric acid, it gave a mixture of benzenepolycarboxylic acids. It was probably a mixture of products from the alkylation of diisopropyl benzene by propylene polymers and from other conversions. The amount of residue usually did not exceed 5 g per 270 – 300 g of alkylate and only with reagent ratios close to equimolecular, did it rise to 16 – 20 g. The most characteristic experiments are presented in the table.

1, 2, 3-Triisopropylbenzene, freed from 1, 3, 5-triisopropylbenzene by many treatments with concentrated sulfuric acid and fractionation on a column with an efficiency of 25 – 30 theoretical plates, was a colorless, mobile liquid, almost without smell:

b.p. 97 – 98° (4 mm), 115 – 117° (15 mm), d_4^{20} 0.8618, n_D^{20} 1.4914, MR_D 68.71; Calc. 67.87. Literature data [1]: b.p. 238.5°, d_4^{20} 0.8613, n_D^{20} 1.4918.

The structure of 1, 2, 4-triisopropylbenzene was confirmed by its conversion into the following derivatives, which are described in [2].

1, 2, 4-Triisopropyl-5-nitrobenzene, obtained in 88% yield by nitration with nitric acid (d 1.52) in acetic acid and anhydride, was isolated in the form of two fractions:

1st b.p. 153 – 155° (12 mm), d_4^{20} 1.0068, n_D^{20} 1.5172; 2nd b.p. 156 – 160° (12 mm), d_4^{20} 1.0034, n_D^{20} 1.5190.

1, 2, 4-Triisopropyl-5-aminobenzene was obtained in 92% yield by reduction of the two fractions with iron and hydrochloric acid in alcohol: b.p. 121 – 122° (3 mm), d_4^{20} 0.9201, n_D^{20} 1.5219. 2, 4, 5-Triisopropylacetanilide: m.p. 140.5 – 141.5° (from aqueous alcohol). 2, 4, 5-Triisopropylbenzanilide: m.p. 158 – 159° (from isopropyl alcohol).

Oxidation of triisopropylbenzenes with nitric acid. Triisopropylbenzene, freed from the light-boiling isomer by fractionation and preliminary treatment with sulfuric acid, was oxidized with 20 – 30% nitric acid to give 20% of monobasic 3, 4-diisopropylbenzoic acid with m.p. 145.5 – 146° and 25% of a mixture of trimellitic and isopropylbenzenedicarboxylic acids. The absence of trimesic acid from the oxidation products indicates that this triisopropylbenzene did not contain 1, 3, 5-triisopropylbenzene.

In the oxidation of triisopropylbenzenes, isolated from the alkylate by the usual fractionation, without preliminary treatment with sulfuric acid, in addition to the acids given above, we also obtained trimesic acid in a yield of 17 – 19% on the original hydrocarbon. Since, under analogous conditions, the symmetrical triisopropylbenzene was 91 – 95% oxidized by nitric acid, it can be assumed that the triisopropylbenzene, obtained by alkylation of p-diisopropylbenzene with propylene, contained 18 – 20% of 1, 3, 5-triisopropylbenzene in addition to 1, 2, 4-triisopropylbenzene.

1, 2, 4, 5-Tetraisopropylbenzene formed white needles; after recrystallization from alcohol the product melted at 117 – 118°, which agrees with literature data in [1].

SUMMARY

A study was made of the alkylation of p-diisopropylbenzene with propylene in the presence of $BF_3 \cdot H_3PO_4$ catalyst.

Conditions were found under which triisopropylbenzenes were obtained in 81% of theoretical yield. The triisopropylbenzenes were a mixture of products, consisting of 80 – 82% of 1, 2, 4-triisopropylbenzene and 18 – 20% of 1, 3, 5-triisopropylbenzene.

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METHOD OF PREPARING DIALKYLTHIOPHOSPHINIC ACIDS

T. A. Mastryukova, A. É. Shipov and M. I. Kabachnik

Institute of Organoelement Compounds, Academy of Sciences, USSR

The dialkylthiophosphinic acids, R_2PSOH, have not been studied. The literature contains data on two representatives of this class of substance. Dibenzylthiophosphinic acid was described by Strecker and Grossman [1] as a side product in the reaction of phosphorus thiochloride with benzylmagnesium chloride. By the reaction of phosphorus thiochloride with ethylmagnesium bromide they isolated a crystalline substance with m.p. 76°, to which they ascribed the formula of diethylthiophosphinic acid. Esters of dialkylthiophosphinic acids and some of their salts have been studied in more detail [2, 3].

In connection with an investigation of the thione-thiol tautomerism of organothiophosphorus compounds [4, 5], it seemed interesting to prepare dialkylthiophosphinic acids with various radicals at the phosphorus and to study some of their properties. With this aim, we developed a method of synthesizing these substances, basing it on the following data.

In 1951 Kosolapoff and Watson [6] published a method of preparing dialkylphosphinic acids, consisting of the action of a Grignard reagent on a dialkyl phosphite with subsequent oxidation of the dialkylphosphinous acid formed with hydrogen peroxide by the scheme:

$$(RO)_2PHO + 3R'MgX \longrightarrow R'_2POMgX + 2ROMgX + R'H$$

$$R'_2POMgX + HCl \longrightarrow R'_2PHO + MgXCl$$

$$R'_2PHO + H_2O_2 \longrightarrow R'_2POOH + H_2O$$

The dialkylphosphinic acids formed were purified by conversion into acid chlorides. Kosolapoff and Watson did not isolate the free dialkylphosphinic acids. These reactions were studied in more detail by Williams, Hamilton et al. [7 – 9], who used them for the preparation of dialkylphosphinous and dialkylphosphinic acids.

The intermediate products of the reactions presented above are magnesium salts of dialkylphosphinous acids. We found that like the salts of dialkylphosphorous acids [10, 11, 4], these salts added sulfur with the formation of magnesium salts of dialkylthiophosphinic acids, from which the free acid was readily isolated. The method of synthesis presented below was based on this and the general scheme of it may be represented by the following equations:

$$(RO)_2PHO + 3R'MgX \longrightarrow R'_2POMgX + 2ROMgX + R'H$$

$$R'_2POMgX + S \longrightarrow R'_2PSOMgX$$

$$R'_2PSOMgX + HCl \longrightarrow R'_2PSOH + 2MgXCl$$

In practise, sulfur was added to an ether solution of the magnesium salt of the dialkylphosphinous acid, formed from a dialkylphosphite and a Grignard reagent. The sulfur dissolved readily with the evolution of heat to give the magnesium salt of a dialkylthiophosphinic acid. Acidification of the reaction mixture with aqueous hydrochloric acid liberated the free dialkylthiophosphinic acid, which passed into the ether layer.

The table gives the constants, neutralization equivalents, elementary analysis data and yields of the acids obtained. That dialkylthiophosphinic acids were actually formed by the scheme presented above was demonstrated by synthesis using the example of dipropylthiophosphinic acid.

Using the method of one of us and Tsvetkov [12], the dibutyl ester of propylphosphinous acid was prepared from dibutyl chlorophosphite and propylmagnesium bromide – $(C_4H_9O)_2PCl + C_3H_7MgBr \rightarrow (C_4H_9O)_2PC_3H_7 + MgBrCl$. This ester was isomerized by Arbuzov's method in the presence of propyl bromide to give the butyl ester of dipropylphosphinic acid – $(C_4H_9O)_2PC_3H_7 + C_3H_7Br \rightarrow (C_3H_7)_2PO(OC_4H_9) + C_4H_9Br$; the acid chloride was prepared from this [13] – $(C_3H_7)_2PO(OC_4H_9) + PCl_5 \rightarrow (C_3H_7)_2POCl + C_4H_9Cl + POCl_3$. When heated with phosphorus pentasulfide [14], this acid chloride was converted into the acid chloride of dipropylthiophosphinic acid – $5(C_3H_7)_2POCl + P_2S_5 \rightarrow 5(C_3H_7)_2PSCl + P_2O_5$.

Hydrolysis of the acid chloride of the thiophosphinic acid gave dipropylthiophosphinic acid, from which we prepared the ammonium salt with m.p. 116.5 – 118.5°. A mixed melting point with the ammonium salt of the free acid, synthesized by the method described in the present work, was not depressed (m.p. 117 — 119°).

The diethylthiophosphinic acid we prepared appeared as a readily distillable liquid, which crystallized only on freezing, in contrast to the preparation of Strecker and Grossmann, for which they reported m.p. 76° [1]. We repeated Strecker and Grossmann's synthesis, exactly according to their description and isolated a substance with m.p. 76°, however, it did not dissolve in alkali without decomposition. A more detailed investigation showed that the substance with m.p. 76° was tetraethyldithiodiphosphyl, $(C_2H_5)_2P(S)P(S)-(C_2H_5)_2$. The latter is a homolog of tetramethyldithiophosphyl, which one of us and E. S. Shepeleva [15] obtained previously by the reaction of methylmagnesium iodide with phosphorus thiochloride.

EXPERIMENTAL

Preparation of dialkylphosphinic acids. In an atmosphere of nitrogen and with vigorous stirring and cooling, to the Grignard reagent prepared from 0.65 g-at of magnesium and 0.69 mole of alkyl halide in 200 ml of ether was gradually added 0.2 mole of diethyl phosphite at such a rate that the ether boiled. The reaction mixture was then heated on a water bath for 1 hour and after this, excess sulfur (0.25 mole) was added in portions with vigorous stirring. Here also the ether boiled. After the addition of the sulfur, the reaction mixture was heated on a water bath for 1 hour. The contents of the flask

Expt. No. n. n.	Formula	B. p. (pressure in mm)	M. p.	Neutralization equivalent**** found	Neutralization equivalent**** calc.	% C found	% C calc.	% H found	% H calc.	% P found	% P calc.	Yield (in %)
1	$(C_2H_5)_2PSOH$*	88.5—89° (1.5)	11.5°**	138.1, 138.0	138.2	34.60, 34.46	34.76	7.59, 7.89	8.02	22.35, 22.10	22.41	69
2	$(C_3H_7)_2PSOH$	98.5—99 (2)	31**;	166.3, 166.0	166.2	43.45, 43.52	43.35	9.42, 9.36	9.10	18.66, 18.93	18.63	81
3	$(iso\text{-}C_3H_7)_2PSOH$	—	76—77.5	166.2, 166.3	166.2	43.60, 43.57	43.35	9.10, 9.16	9.10	—	—	64
4	$(C_4H_9)_2PSOH$	81—81.5 ($2.5 \cdot 10^{-2}$)	—	193.9, 193.9	194.3	49.39, 49.25	49.45	9.83, 9.95	9.86	16.04, 16.15	15.94	74
5	$(iso\text{-}C_4H_9)_2PSOH$	—	69.5—70.5	194.2, 194.4	194.3	49.38, 49.48	49.45	9.80, 9.78	9.86	16.34, 16.15	15.94	69
6	$(C_6H_5CH_2)_2PSOH$***	—	190.5—191.5	262.2, 262.6	262.3	64.29, 64.22	64.10	5.82, 5.83	5.78	—	—	72

* n_D^{20} 1.5262, d_4^{20} 1.1090.

** Thermometer in mass.

*** Literature data [1]: m.p. 171°.

**** Thymolphthalein as indicator.

were cooled and decomposed with hydrochloric acid (1 : 1) with stirring until the precipitate dissolved completely (the temperature inside the flask during the addition of the acid was not allowed to exceed 20°). The reaction mixture separated into three layers, which changed into two on addition of water. The ether layer was separated, the aqueous one extracted with ether and the bulk of the ether distilled from the combined ether extracts. To the residue was added 100 ml of water and the mixture made alkaline to litmus with sodium carbonate. The insoluble part was extracted with ether, the aqueous solution treated with excess hydrochloric acid and the liberated acid extracted with benzene. The benzene solution was dried with sodium sulfate and fractionated in vacuum. The dialkylthiophosphinic acids were obtained in 64 – 88% yield (see Table).

Diethylthiophosphinic and dipropylthiophosphinic acids were also obtained by the action of Grignard reagents on dibutyl phosphite in the same molar ratios. The yields of the acids were 50 and 84%, respectively.

The dibutyl ester of propylphosphinous acid was obtained by the method described [12].

B.p. 93.5 – 95° (7 mm), n_D^{20} 1.4400, d_4^{20} 0.8844. Yield 70%. Literature data [12]: b.p. 59.8 – 60.3° (1 mm), n_D^{20} 1.4393, d_4^{20} 0.8851.

The butyl ester of dipropylphosphinic acid was obtained by an Arbuzov rearrangement of the dibutyl ester of propylphosphinous acid with propyl bromide (3 hours at 160°). The yield was 80.8%.

B.p. 78 – 79° (1 mm), n_D^{20} 1.4389, d_4^{20} 0.9343, MR_D 58.07; Calc. 58.12.

Found %: C 58.30, 58.28; H 11.22, 11.27; P 14.77, 14.47. $C_{10}H_{23}O_2P$. Calculated %: C 58.23; H 11.24; P 15.01.

The acid chloride of dipropylphosphinic acid was obtained by reaction of the butyl ester of dipropylphosphinic acid with phosphorus pentachloride. The yield was 81%.

B.p. 110.5 – 112° (8 mm), n_D^{20} 1.4662, d_4^{20} 1.0689. Literature data [13]: b.p. 118.5 – 120° (11 mm), n_D^{20} 1.4667, d_4^{20} 1.0692.

The acid chloride of dipropylthiophosphinic acid was obtained by heating the acid chloride of dipropylphosphinic acid with phosphorus pentasulfide [14] at 135 – 150° for 2 hours. The yield was 59%.

B.p. 107 – 109° (7 mm), n_D^{20} 1.5190, d_4^{20} 1.0845, MR_D 51.66; Calc. 51.56. Literature data [16]: b.p. 131 – – 135° (15 mm).

Found %: C 38.83, 38.96; H 7.55, 7.57; P 16.84, 16.71; Cl 19.29, 19.03. $C_6H_{14}PSCl$. Calculated %: C 39.04; H 7.64; P 16.78; Cl 19.21.

Ammonium dipropylthiophosphinate. a) 10 g of the acid chloride of dipropylthiophosphinic acid was heated for 1.5 hours in a stream of nitrogen with 6.17 g of potassium hydroxide in 100 ml of 70% aqueous alcohol. After separation of the precipitate and removal of the solvent, the residue was dissolved in water, the neutral impurities extracted with ether, the solution acidified with concentrated hydrochloric acid, the liberated dipropylthiophosphinic acid extracted with benzene and, when the solution had been dried with sodium sulfate, the ammonium salt precipitated with a stream of dry ammonia. We obtained 5.3 g (54%) of ammonium dipropylthiophosphinate with m.p. 116.5 – 118.5°.

b) Into a solution of 6.15 g of dipropylthiophosphinic acid, obtained by the general method given above, in 50 ml of dry petroleum ether, was passed a stream of ammonia. We obtained 6.52 g (96%) of ammonium dipropylthiophosphinate with m.p. 117 – 119°. The melting point of a mixture with the sample obtained by procedure "a" was 117 – 119°.

Tetraethyldithiodiphosphyl. To a solution of the Grignard reagent, obtained from 9.6 g of magnesium and 38 g of ethylbromide in 150 ml of ether, was gradually added 8 g of $PSCl_3$ in 25 ml of ether with cooling. The reaction product was poured in small portions into cooled sulfuric acid with ice (1 : 1). The organic layer was separated, the aqueous one extracted with ether and the combined extracts dried over anhydrous sodium sulfate. After removal of the ether, the residue was recrystallized from petroleum ether. We obtained 2 g of a substance with m.p. 76 – 77°. The substance was not titrated by alkali in the cold, but dissolved in 20% aqueous sodium hydroxide on heating.

Found %: C 39.42, 39.52; H 8.30, 8.23; P 25.43, 25.23; S 26.50, 26.65. M 237.3, 240.2 (cryoscopically in benzene). $C_8H_{20}S_2P_2$. Calculated %: C 39.65; H 8.32; P 25.51; S 26.46. M 242.3.

SUMMARY

1. A method was developed for synthesizing dialkylthiophosphinic acids, R_2PSOH, by the action of a Grignard reagent on dialkylphosphorous acids with the subsequent addition of sulfur.

2. This method yielded the acids R_2PSOH (R = C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9, iso-C_4H_9 and $C_6H_5CH_2$) in yields of 64 – 88%.

3. The structure of the dialkylthiophosphinic acids obtained by the new method was confirmed by synthesis of the ammonium salt of dipropylthiophosphinic acid.

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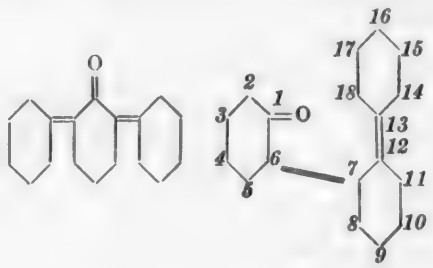
• • In Russian.

LOW-TEMPERATURE AUTOCONDENSATION OF CYCLOHEXANONE

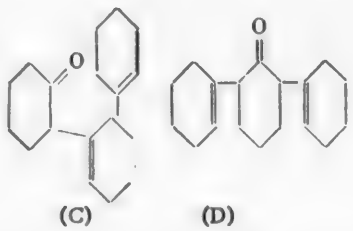
S. V. Svetozarskii, E. N. Zil'berman and G. A. Razuvaev

The autocondensation of cyclohexanone yields 2-cyclohexylidenecyclohexanone [1] and tricyclic [2 — 6] products, containing one carbonyl group. The products of the formula $C_{18}H_{26}O$ were first isolated by Wallach [2] from products obtained by keeping cyclohexanone in contact with sodium ethylate for many days. Condensation of cyclohexanone in the presence of a methanol solution of sulfuric acid [3] yielded a liquid product of the same empirical formula, to which was assigned the structure of 2, 6-dicyclohexylidenecyclohexanone (A). Together with this, there was also formed a small amount of dodecahydrotriphenylene. By the reaction of cyclohexanone and 2-cyclohexylidenecyclohexanone with the addition of sodium hydroxide solution, Kunze [4] obtained dodecahydrotriphenylene and on the basis of this, he proposed that a compound of structure (B) was formed as an intermediate in this reaction.



(A) (B)

Heating cyclohexanone in the presence of solid potassium hydroxide [5] gave (29% yield) a crystalline compound with m.p. 79° and structure (C) was proposed for it. However, Plevsek conclusively showed that this compound had the structure of 2, 6-dicyclohexenylcyclohexanone (D). Recently, a product isomeric with (D) and having structure (A) was synthesized [7].



(C) (D)

All the products obtained in the autocondensation of cyclohexanone were unsaturated ketones. Their formation could be explained readily by the intermediate formation of the corresponding tertiary alcohols, which readily lose water and are converted into unsaturated ketones. However, there is no information on the synthesis of such tertiary alcohols in the literature.

In the present work we used the autocondensation of cyclohexanone at room temperature in the presence of solid sodium hydroxide as catalyst to prepare a compound of the formula $C_{18}H_{30}O_3$ (I), which was a tricyclic product with one carbonyl group and two tertiary hydroxyl groups.

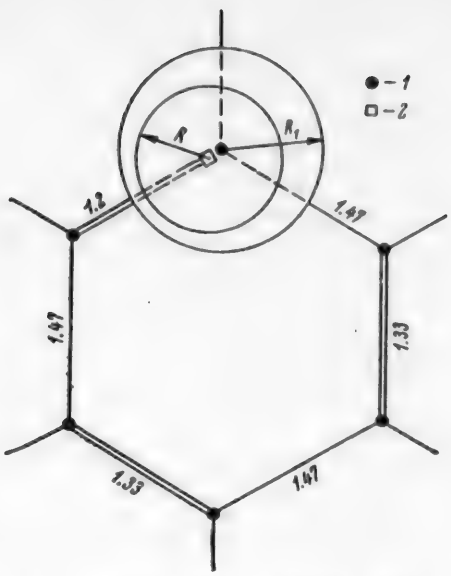


Fig. 1. 1) Carbon atoms, 2) oxygen atom, R and R_1 — covalent radii of oxygen and carbon atoms.

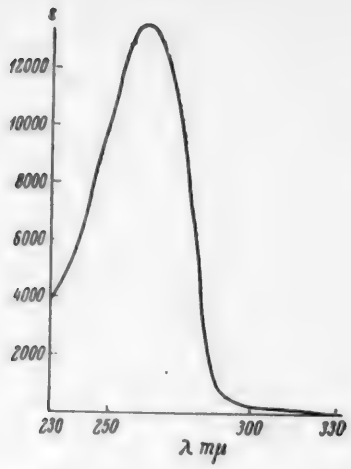
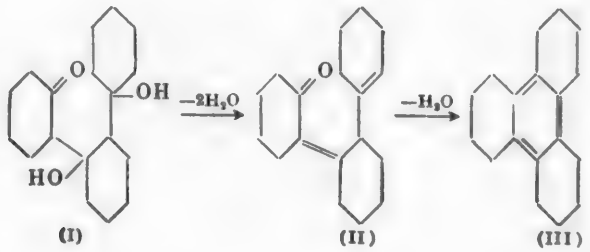


Fig. 2. Ultraviolet spectrum of ketone (II) in diethyl ether.

When heated with solid sodium hydroxide, (I) was decomposed into cyclohexanone and 2-cyclohexylidenecyclohexanone. The interaction of (I) with concentrated sulfuric acid, and also heat for a short time, eliminated two molecules of water and formed an unsaturated ketone with the formula $C_{18}H_{26}O$ (II). Treatment of (I) with benzoyl chloride by the Schotten-Baumann method did not yield an ester. Instead, we obtained ketone (II), mentioned above. Prolonged heating of (I) and also of (II) gave a high yield of dodecahydro-1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12-triphenylene (III). On the basis of the conversion of (I) into (III), compound $C_{18}H_{30}O_3$ must be a dihydroxyketone and have the structure of 2-[2-(1--hydroxycyclohexyl)-1-hydroxycyclohexyl]-cyclohexanone. The molecule of ketone (II) contains one carbonyl group and two double bonds. The structure (B) must be considered inadmissible since the carbon atoms 1, 6, 7, 12, 13 and 18 and the oxygen atom in it would be in one plane and then the covalent radii of the oxygen and C_{18} would overlap each other (Fig. 1). Evidently, steric factors are the reason for the comparatively easy conversion of (II) into (III). The ultraviolet spectrum in diethyl ether (Fig. 2) was used to define the structure of ketone (II). The observed absorption maximum (λ_{max} 263 mμ, ϵ_{max} 13,500) is characteristic of α, β, β-substituted α, β-unsaturated ketones [8] and close to the absorption maximum of 2-cyclohexylidenecyclohexanone [1]. On the basis of this, structure (C) and certain other variations were also excluded for ketone (II) and it could only be 2-[2-(Δ'-cyclohexenyl)-cyclohexylidene]-cyclohexanone. The usual derivatives of carbonyl compounds were not obtained from ketone (II) or from the dihydroxyketone (I) either and in this case this may be explained readily by steric hindrance.



It should be noted that (III) is usually obtained in a yield that does not exceed 6% [3]. The conversions of (I) and (II) into (III) we described are a convenient method of preparing dodecahydrotriphenylene.

We take this opportunity to thank Ts. N. Roginskaya for plotting the ultraviolet spectra.

EXPERIMENTAL

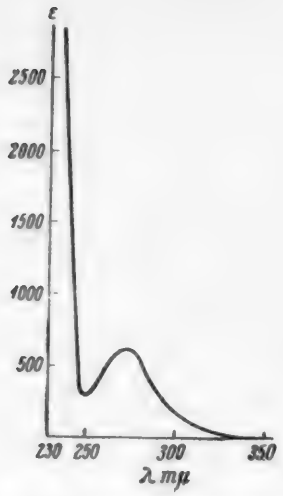


Fig. 3. Ultraviolet spectrum of dodecahydrotriphenylene (III) in ethyl alcohol.

2-[2-(1-Hydroxycyclohexyl)-1-hydroxycyclohexyl]-cyclohexanone (I). A mixture of 20 g of finely powdered sodium hydroxide and 200 g of cyclohexanone was left to stand for 72 hours with ocasional stirring. The yellowish paste formed was washed with water until neutral. To the white paste was added 200 ml of methyl alcohol and the mixture stirred. The white precipitate liberated was collected, washed with 100 ml of methyl alcohol and dried. We obtained 80 g (40%) of (I) in the form of a fine white powder with m.p. 175° (from benzene). Substance (I) was insoluble in water, difficultly soluble in methyl alcohol and acetone and more soluble in benzene and pyridine.

Found %: C 73.53, 73.67; H 10.19, 10.20. M 297. $C_{18}H_{30}O_3$. Calculated %: C 73.42; H 10.21. M 294.

100 g of (I) and 10 g of solid sodium hydroxide were heated for 1 hour at 200°. Distillation of the red liquid obtained yielded 24.7 g (74%) of cyclohexanone with b.p. 67° (40 mm), n_D^{20} 1.4510 and 49.3 g (81.5%) of 2-cyclohexylidenecyclohexanone with b.p. 124° (5 mm), n_D^{20} 1.5056.

2-[2-(Δ'-Cyclohexenyl)-cyclohexylidene]-cyclohexanone (II). a) A mixture of 17.2 g of (I) and 13 ml of concentrated sulfuric acid was left to stand for 12 hours. The thick red oil formed was poured into water and extracted with ether. The ether solution was washed with water until neutral and evaporated to yield a yellowish oil, which solidified completely on standing for 6 days or in 1 hour after washing with methyl alcohol. The solid product was ground, washed with methyl alcohol and dried in air. We obtained 14 g (92.7%) of substance (II) in the form of a fine white powder with m.p. 44°. Substance (II) was insoluble in water, difficultly soluble in methyl alcohol and acetone and more soluble in benzene, pyridine and ether.

Found %: C 84.09, 83.90; H 10.14, 10.13. M 260. $C_{18}H_{26}O$. Calculated %: C 83.75; H 10.07. M 258.

b) A mixture of 50 ml of methyl alcohol, 6 ml of concentrated sulfuric acid and 10 g of (I) was left to stand for 1 hour. Washing the white paste formed with water until neutral and allowing it to stand for 1 hour yielded 7.7 g (88%) of substance (II).

c) To a solution of 10 g of (I) in 100 ml of pyridine was added 10 ml of benzoyl chloride. When it had cooled to room temperature, the solution was heated to 80°. As it stood, the reaction mixture deposited long, fine, yellowish platelets, which were unstable in air. The yellow oil, formed when the reaction mixture was poured into water, solidified on standing for 3 days. We obtained 6.7 g (77%) of ketone (II).

d) 25 g of (I) was heated at 350° for 1 hour. Washing the yellow oil formed with methyl alcohol yielded 4 g (18.5%) of ketone (II).

Dodecahydro-1,2,3,4,5,6,7,8,9,10,11,12-triphenylene (III). a) 16 g of (II) was heated to 350° for 2 hours. On cooling, almost the whole of the product solidified. Washing the brownish mass with a small amount of benzene yielded 11 g (73.8%) of (III) with m.p. 232° (from benzene), which did not depress the melting point of (III) synthesized by Mannich's method [3]. The ultraviolet spectrum in ethyl alcohol (Fig. 3) was identical with the ultra violet spectrum of the same compound, described in [9].

b) 23 g of (I) was heated at 350° for 4 hours. After cooling, the almost solid brown mass was treated as described above and we obtained 15.5 g (73.5%) of hydrocarbon (III).

c) 13 g of (I) was heated at 350° for 2 hours. The yellow oil formed was dissolved with heating in 50 ml of glacial acetic acid and a stream of dry hydrogen chloride passed through it for 1 hour. The solid product liberated was collected. Dry hydrogen chloride was passed into the filtrate for another hour, which gave an additional amount of the solid compound. In all, we obtained 9.6 g (90.5%) of hydrocarbon (III).

SUMMARY

1. Autocondensation of cyclohexanone under normal conditions in the presence of solid sodium hydroxide yielded a tricyclic product with one carbonyl and two tertiary hydroxyl groups and which had the structure of 2-2-[2-(1-hydroxycyclohexyl)-1-hydroxycyclohexyl]-cyclohexanone.

2. Successive elimination of two and one molecules of water from the dihydroxyketone yielded the previously undescribed unsaturated ketone, 2-[2-(Δ'-cyclohexenyl)-cyclohexylidene]-cyclohexanone and dodecahydrotriphenylene, respectively.

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TETRAACYLOXYSILANES IN ORGANIC SYNTHESIS

XX. SYNTHESIS OF β-DIKETONES BY ACYLATION OF MALONIC AND ACETOACETIC ESTERS WITH TETRAACYLOXYSILANES

Yu. K. Yur'ev and Z. V. Belyakova

Moscow State University

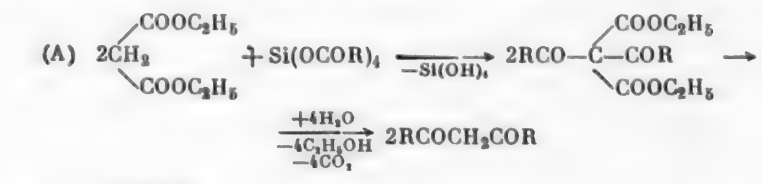
As is known, β-diketones are obtained by acylation of ketones with acid esters in the presence of strongly alkaline agents, sodamide (57 – 76% yields) [1 — 3], sodium [4 — 7], sodium hydride (45 – 51% yields) [8] and lithium hydride (50 – 76% yields) [9], by acylation of ketones with acid anhydrides in the presence of boron trifluoride (22 – 83% yields) [10] or zinc chloride (4.7 – 47.5% yields) [11] and also by ketonic cleavage of C-acylated derivatives of acetoacetic ester [12]. Dibenzoylmethane was obtained in 20% yield by the action of sodium ethylate onethyl benzoate [13]. Descriptions are also given of the preparation of β-diketones by acylation of vinyl acetate with acid chlorides in the presence of anhydrous aluminum chloride (6 – 31% yields) [14] and by catalytic or thermal isomerization of enol acetates [15].

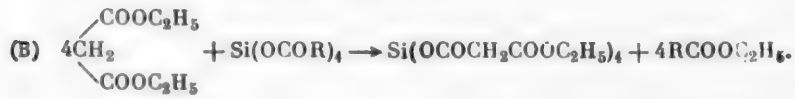
An interesting method of synthesizing β-diketones of the type $RCOCH_2COR$ consists of acylating malonic ester with acid anhydrides in the presence of magnesium oxide or copper acetate as catalysts (50 – 60% yields) [16]. In the present work, we studied the possibility of using silicoanhydrides of monobasic organic acids in this reaction and by acylating malonic ester with them in the presence of magnesium oxide and copper acetate at 165 – 170°, we obtained 34 – 37% yields of the following β-diketones: pentanedione-2, 4, heptanedione-3, 5, nonanedione-4, 6, undecanedione-5, 7, 2, 8-dimethylnonanedione-4, 6 and tridecanedione-6, 8. We could not obtain 2, 7-dimethylheptanedione-3, 5 from the silicoanhydride of isobutyric acid. By the action of silicobenzoic anhydride on malonic ester, we obtained dibenzoylmethane in 19% yield.

The course of the reaction described for the preparation of β-diketones of the type $RCOCH_2COR$ may be represented by the following schemes.

1. The acylating agent is an acid anhydride, arising during the reaction process by thermal decomposition of the silicoanhydride and reacting with malonic ester as described above [16].

2. Acylation of malonic ester produces a silicoanhydride of a monobasic organic acid, forming, on one hand, a diacyl derivative of malonic ester and silicic acid (A) and on the other, the silicoanhydride of the acid ethyl ester of malonic acid and the ethyl ester of the organic acid, forming part of the silicoanhydride (B).





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That the second scheme for the reaction mechanism is correct is confirmed by our observation that it is possible to acylate malonic ester with the silicoanhydrides of acetic, propionic and isovaleric acids under conditions which exclude the possibility of the formation of anhydrides from them, namely, at 50 – 100° in the presence of anhydrous stannic chloride. In this case the yield of the copper salt of pentanedione-2, 4 was 16%, of heptanedione-3, 5, 18% and of 2, 8-dimethylnonanedione-4, 6, 25%. The formation of ethyl isovalerate together with 2, 8-dimethylnonanedione-4, 6 in the acylation of malonic ester with silicoisovaleric anhydride in the presence of stannic chloride convincingly illustrates that the reaction proceeds in the two directions considered in the second scheme and again confirms the accuracy of this scheme for the reaction mechanism.

In the present work, a method was also developed for the synthesis of β-diketones of the type CH_3COCH_2COR, which consists of acylating acetoacetic ester with silicoanhydrides of saturated monobasic organic acids under the same conditions with the subsequent ketonic cleavage of the C-acyl derivative of acetoacetic ester obtained. In this way we obtained 34.5 – 77% yields of the following β-diketones: pentanedione-2, 4, hexanedione-2, 4, heptanedione-2, 4, 6-methylheptanedione-2, 4 and nonanedione-2, 4. In accordance with the previous mechanism, this reaction is represented by the following scheme:

$$(A)\quad 4CH_3COCH_2COOC_2H_5 + Si(OCOR)_4 \xrightarrow[-Si(OH)_4]{} 4CH_3COCHCOOC_2H_5 \xrightarrow{+H_2O}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad COR$$
$$\longrightarrow 4CH_3COCH_2COR + 4CO_2 + 4C_2H_5OH$$
$$(B)\quad 4CH_3COCH_2COOC_2H_5 + Si(OCOR)_4 \longrightarrow Si(OCOCH_2COCH_3)_4 + 4RCOOC_2H_5$$

In the example of the acylation of acetoacetic ester, it was shown that the yields of β-diketones were increased by changing the ratio of acid (in the silicoanhydride) to aceloacetic ester from 1 : 1 to 2 : 1. Thus, 6-methylheptanedione-2, 4 was obtained in 77% yield with a reagent ratio of 2 : 1 and 42% ar a ratio of 1 : 1; nonanedione-2, 4 was obtained in yields of 51 and 43%, respectively.

In preparing β-diketones of the type CH_3COCH_2COR by acylation of acetoacetic ester with tetraacyloxysilanes, it was not always advantageous to isolate them in the form of copper salts. It was found that slow distillation gave quite pure β-diketones in higher yield. The lower yield of β-diketones when they were isolated through the copper salts was evidently connected with incompleteness of formation of the copper salt from a mixture of β-diketone and the corresponding ester.

EXPERIMENTAL

Acylation of Malonic Ester with Tetraacyloxysilanes in the Presence of Magnesium Oxide and Copper Acetate

Into a three-necked flask with a stirrer and a reflux condenser with a calcium chloride tube were placed 0.4 mole of acid and 0.12 mole of silicon tetrachloride and the mixture heated for 5 - 6 hours on a water bath until the evolution of hydrogen chloride ceased. Traces of the latter and unchanged silicon tetrachloride were removed by passing dry air through the mixture. Then to the silicoanhydride were added 0.5 g of magnesium oxide, 0.5 g of copper acetate and 0.1 mole of malonic ester and the mixture heated on an oil bath at 165 - 170° for 8 hours. The mixture was cooled, broken down with 50 ml of 10% sulfuric acid and the reaction product steam distilled. The distillate was extracted with ether and the extracts dried with anhydrous sodium sulfate. The ether was removed and to the residue was added a saturated aqueous solution of copper acetate. The precipitated copper salt was collected by filtration. The organic layer of the filtrate was separated and the corresponding ester distilled from it; a further amount of copper salt was obtained in the residue. The copper salt was decomposed in ether with 20% sulfuric acid; the ether extracts were dried, the ether removed and the β-diketone obtained distilled.

Pentanedione-2, 4. From 24 g of acetic acid, 20.4 g of silicon tetrachloride and 16 g of malonic ester we obtained 4.5 g (34.5%) of copper salt and 1.2 g of ethyl acetate with b.p. 75 – 77° (752 mm), n_D^{20} 1.3730 and d_4^{20} 0.9015. The copper salt (it did not melt) yielded 3.4 g (99%) of pentanedione-2, 4:

b.p. 68° (70 mm), n_D^{20} 1.4510, d_4^{20} 0.9780.
Literature data [17]: b.p. 137°, d_4^{20} 0.976, n_D^{20} 1.4510.

Heptanedione-3, 5. From 29.6 g of propionic acid, 20.4 g of silicon tetrachloride and 16 g of malonic ester we obtained 5.7 g (36%) of a copper salt with m.p. 209 – 210° (from acetone) and 2 g of ethyl propionate with b.p. 97 – 99° (748 mm), n_D^{20} 1.3835, and d_4^{20} 0.8913.

The copper salt yielded 4.5 g (98.5%) of heptanedione-3, 5:

b.p. 79 – 80° (30 mm), n_D^{20} 1.4568, d_4^{20} 0.9458.
Literature data: b.p. 172 – 173° (711 mm), d_4^{20} 0.9445 [4], b.p. 78 – 81° (30 mm), copper salt; m.p. 209 – 210° [9].

Nonanedione-4, 6. From 35.2 g of butyric acid, 20.4 g of silicon tetrachloride and 16 g of malonic ester we obtained 6.9 g (37%) of a copper salt with m.p. 157 – 158° (from acetone) and 12.2 g (1.05 mole) of ethyl butyrate with b.p. 49 – 50° (60 mm), n_D^{20} 1.3925 and d_4^{20} 0.8775; we also obtained 8 g (0.91 mole) of butyric acid with b.p. 95 – 96° (60 mm). The copper salt yield 5.6 g (97.5%) of nonanedione-4, 6:

b.p. 100 – 101° (20 mm), 86° (10 mm), n_D^{20} 1.4606, d_4^{20} 0.9296.
Literature data [11]: b.p. 96 – 99° (20 mm), copper salt; m.p. 157 – 158°.

Undecanedione-5, 7. From 40.8 g of valeric acid, 20.4 g of silicon tetrachloride and 16 g of malonic ester we obtained 8 g (37%) of a copper salt with m.p. 139 – 140° (from acetone), 14.85 g (0.14 mole) of ethyl valerate with b.p. 50 – 52° (18 mm), n_D^{20} 1.3900, d_4^{20} 0.8772, and also 9.3 g (0.91 mole) of valeric acid with b.p. 90 – 91° (18 mm).

Analysis of copper salt:

Found %: C 61.88; H 9.04; Cu 14.62. $C_{22}H_{38}O_4Cu$. Calculated %: C 61.41; H 8.90; Cu 14.77.

From the copper salt we obtained 6.75 g (98.5%) of undecanedione-4, 6:

b.p. 118 – 119° (15 mm), n_D^{20} 1.4621, d_4^{20} 0.9160.

Found %: C 71.69, 71.82; H 11.07, 11.15. $C_{11}H_{20}O_2$. Calculated %: C 71.69; H 10.94.

Literature data [16]: b.p. 81 – 81.5° (8 mm).

2, 8-Dimethylnonanedione-4, 6. From 40.8 g of isovaleric acid, 20.4 g of silicon tetrachloride and 16 g of malonic ester we obtained 7.35 g (34%) of a copper salt with m.p. 157 – 158° (from acetone), 14.7 g (1.13 mole) of ethyl isovalerate with b.p. 62 – 64° (60 mm), n_D^{20} 1.3970 and d_4^{20} 0.8669, and also 11.95 g (1.18 mole) of isovaleric acid with b.p. 108 – 109° (60 mm). The copper salt yielded 6.1 g (97%) of 2, 8-dimethylnonanedione-4, 6:

b.p. 115 – 116° (20 mm), 94° (8 mm), n_D^{20} 1.4555, d_4^{20} 0.9054.
Literature data [9]: b.p. 114 – 116° (20 mm); copper salt: m.p. 157 – 158°.

Tridecanedione-6, 8. From 46.44 g of caprioic acid, 20.4 g of silicon tetrachloride and 16 g of malonic ester we obtained 8.9 g (36.5%) of a copper salt with m.p. 119 – 120° (from acetone), 17.3 g (1.2 mole) of ethyl caproate with b.p. 71 – 73° (32 mm), n_D^{20} 1.4075 and d_4^{20} 0.8733, and also 10 g (0.865 mole) of caproic acid with b.p. 90 – 92° (7 mm). The copper salt yielded 7.6 g (98.5%) of tridecanedione-6, 8:

b.p. 162 – 163° (20 mm), n_D^{20} 1.4609, d_4^{20} 0.9096.
Literature data [9]: b.p. 162 – 165° (20 mm), copper salt: m.p. 119 – 120°.

Dibenzoylmethane. Silicobenzoic anhydride was prepared from 48.8 g of benzoic acid and 20.4 g of silicon tetrachloride in 100 ml of dry benzene. The benzene was removed in vacuum and 16 g of malonic ester, 0.5 g of magnesium oxide and 0.5 g of copper acetate added. The mixture was heated for 8 hours at 165 – 170°, cooled, 100 ml of 10% sulfuric acid added and the mixture heated for 2 hours on a boiling water bath. The precipitate was collected by filtration, the filtrate extracted with ether and the extracts dried with anhydrous sodium sulfate; the ether was removed and the residue distilled. We obtained 13.6 g of ethyl benzoate with b.p. 80° (11 mm), n_D^{20} 1.5050, d_4^{20} 1.0501 and 8.6 g (19%) of dibenzoylmethane:

b.p. 198 – 200° (11 mm), m.p. 77 – 78° (from alcohol); copper salt: m.p. 294 -- 300° (decomp., from alcohol).

Literature data: m.p. 77 – 78° [9]; b.p. 150 – 160° (1 mm), [18] m.p. 77 – 78°; copper salt: m.p. 294 – 301° (with decomp.) [19].

Acylation of Malonic Ester with Tetraacyloxysilanes in the Presence of Anhydrous Stannic Chloride

A mixture of 0.2 mole of organic monobasic acid and 0.06 mole of silicon tetrachloride in 50 ml of dry benzene was heated on a water bath until the evolution of hydrogen chloride ceased. After the addition of 0.1 mole of malonic ester and 26 g (0.1 mole) of anhydrous stannic chloride, the mixture was heated for 3 hours on a water bath at 50 – 60° and for 1 hour on a boiling water bath. Then 50 ml of 10% sulfuric acid was added, the mixture boiled for 2 hours and the reaction product isolated as described above.

Pentanedione-2, 4. From 12 g of acetic acid, 10.2 g of silicon tetrachloride and 16 g of malonic ester we obtained 2.1 g (16%) of the copper salt of pentanedione-2, 4.

Heptanedione-3, 5. From 14.8 g of propionic acid, 10.2 g of silicon tetrachloride and 16 g of malonic ester we obtained 2.85 g (18%) of the copper salt of heptanedione-3, 5: m.p. 209 – 210° (from acetone).

2, 8-Dimethylnonanedione-4, 6. From 20.4 g of isovaleric acid, 10.2 g of silicon tetrachloride and 16 g of malonic ester we obtained 5.4 g (25%) of the copper salt of 2, 8-dimethylnonanedione-4, 6 with m.p. 157 – 158° from acetone and also 6.75 g (0.052 mole) of ethyl isovalerate with b.p. 62 – 64° (60 mm), n_D^{20} 1.3970, d_4^{20} 0.8669 and 3.45 g (0.034 mole) of isovaleric acid with b.p. 107 – 108° (60 mm).

Acylation of Acetoacetic Ester with Tetraacyloxysilanes in the Presence of Magnesium Oxide and Copper Acetate

By the method described above, the silicoanhydride was prepared from 0.2 mole of acid and 0.06 mole of silicon tetrachloride. To it were added 0.5 g of magnesium oxide, 0.5 g of copper acetate and 0.1 – 0.2 mole of acetoacetic ester, the mixture heated for 8 hours on an oil bath at 165 – 170°, cooled and decomposed with 50 ml of 10% sulfuric acid and the reaction product distilled with superheated steam. The distillate was extracted with ether, the extracts dried and the ether removed. Then either a saturated aqueous solution of copper acetate was added to the residue and the copper salt of the β-diketone isolated (method A) or the residue slowly distilled in vacuum and the β-diketone isolated in this way (method B).

Pentanedione-2, 4 (A). From 12 g of acetic acid, 10.2 g of silicon tetrachloride and 13 g (0.1 mole) of acetoacetic ester we obtained 4.5 g (34.5α) of a copper salt and from this, 3.4 g (99%) of β-diketone: b.p. 68° (70 mm), n_D^{20} 1.4510, d_4^{20} 0.9780.

Hexanedione-2, 4 (B). From 14.8 g of propionic acid, 10.2 g of silicon tetrachloride and 13 g (0.01 mole) of acetoacetic ester we obtained 5.6 g (49%) of hexanedione-2, 4:

b.p. 62 – 65° (26 mm), n_D^{20} 1.4525; copper salt m.p. 197 – 198° (from alcohol).

On isolating hexanedione-2, 4 by method A, we obtained 5.5 g (38%) of copper salt with m.p. 197 – 198° (from alcohol) and from that 4.2 g (97.5%) of the β-diketone:

b.p. 62 – 65° (26 mm), n_D^{20} 1.4538, d_4^{20} 0.9514.
Literature data: b.p. 158°, d^{15} 0.9538 [20], $n_D^{14.9}$ 1.4539 [21]; copper salt: m.p. 197 – 198° [22].

Heptanedione-2, 4 (B). From 17.6 g of butyric acid, 10.2 g of silicon tetrachloride and 13 g (0.1 mole) of acetoacetic ester we obtained 2.5 g (0.021 mole) of ethyl butyrate with b.p. 49 – 50° (60 mm), n_D^{20} 1.3927, d_4^{20} 0.9775 and 5.9 g (45.5%) of heptanedione-2, 4: b.p. 57 – 61° (10 mm), n_D^{20} 1.4428, d_4^{20} 0.9400, copper salt m.p. 162 – 163° (from alcohol).

When heptanedione-2, 4 was isolated by method A, we obtained 5.7 g (36%) of copper salt with m.p. 162 – 163° (from alcohol) and 5 g (0.043 mole) of ethyl butyrate with b.p. 49 – 50° (60 mm), n_D^{20} 1.3925, d_4^{20} 0.8775. The copper salt yielded 4.5 g (98%) of heptanedione-2, 4:

b.p. 57 – 60° (10 mm), n_D^{20} 1.4458, d_4^{20} 0.9409.
Literature data [23]: b.p. 175 – 176° (740 mm), d_4^{20} 0.9410, n_D^{20} 1.4539; copper salt m.p. 162 – 163°.

6-Methylheptanedione-2, 4 (B). a) From 20.4 g of isovaleric acid, 10.2 g of silicon tetrachloride and 13 g (0.1 mole) of acetoacetic ester we obtained 4 g (0.03 mole) of ethyl isovalerate with b.p. 62 – 64° (60 mm), n_D^{20} 1.3972, d_4^{20} 0.8669 and 10.9 g (77%) of 6-methylheptanedione-2, 4 with b.p. 75 – 77° (20 mm), n_D^{20} 1.4370, d_4^{20} 0.9203; the copper salt had m.p. 142 — 143° (from alcohol).

b) From 20.4 g of isovaleric acid, 10.2 g of silicon tetrachloride and 26 g (0.2 mole) of acetoacetic ester we obtained 5 g (0.038 mole) of ethyl isovalerate with b.p. 62–64° (60 mm), n_D^{20} 1.3972 and 12 g (42%) of 6-methylheptanedione-2, 4:

b.p. 75–77° (20 mm), n_D^{20} 1.4375; copper salt m.p. 142–143° (from alcohol).
Literature data [12]: b.p. 76° (19 mm), d_4^{20} 0.936; copper salt m.p. 142°.

Nonanedione-2, 4 (B). a) From 23.2 g of caproic acid, 10.2 g of silicon tetrachloride and 13 g (0.1 mole) of acetoacetic ester we obtained 1.5 g (0.01 mole) of ethyl caproate with b.p. 71–73° (30 mm), n_D^{20} 1.4070, d_4^{20} 0.8735 and 8 g (51%) of nonanedione-2, 4 with b.p. 105–107° (22 mm), n_D^{20} 1.4338, d_4^{20} 0.9208; the copper salt had m.p. 132–134° (from alcohol).

b) From 23.2 g of caproic acid, 10.2 g of silicon tetrachloride and 26 g (0.2 mole) of acetoacetic ester we obtained 6.2 g (0.043 mole) of ethyl caproate with b.p. 71–73° (30 mm), n_D^{20} 1.4072, d_4^{20} 0.8735 and 13.5 g (43%) of nonanedione-2, 4:

b.p. 105–107° (22 mm), n_D^{20} 1.4338; copper salt m.p. 132–134° (from alcohol).
Literature data [12]: b.p. 100° (20 mm); copper salt m.p. 136°.

SUMMARY

1. Acylation of malonic ester with silicoanhydrides of saturated monobasic organic acids in the presence of magnesium oxide and copper acetate or stannic chloride led to β-diketones of the type $RCOCH_2COR$. By this method we prepared pentanedione-2, 4, heptanedione-3, 5, nonanedione-4, 6, undecanedione-5, 7, 2, 8-dimethylnonanedione-4, 6, tridecanedione-6, 8 and dibenzoylmethane.

2. Acylation of acetoacetic ester with silicoanhydrides of saturated monobasic organic acids in the presence of magnesium oxide and copper acetate with subsequent ketonic cleavage led to β-diketones of the type CH_3COCH_2COR. By this method we prepared pentanedione-2, 4, hexanedione-2, 4, heptanedione-2, 4, 6-methylheptanedione-2, 4 and nonanedione-2, 4.

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TETRAACYLOXYSILANES IN ORGANIC SYNTHESIS

XXI. PREPARATION OF ACYLOXYTRICHLOROSILANES FROM ACIDS OF AN AROMATIC NATURE

Yu. K. Yur'ev, Z. V. Belyakova and V. P. Volkov

Moscow State University

By boiling benzoic acid for 12 hours in excess silicon tetrachloride, in previous work two of us [1] prepared benzoyloxytrichlorosilane, a representative of a yet unstudied class of acyloxytrichlorosilanes, which are mixed anhydrides, formed from three acids, namely, silicic, a monobasic organic and hydrochloric acids.

In the present work we established that homologs of benzoic acid (o- and p-toluic), α-naphthoic and substituted benzoic acids (o- and p-chlorobenzoic and o-, m- and p-nitrobenzoic) and also α-furancarboxylic and α-thiophenecarboxylic acids reacted with excess silicon tetrachloride to give a quantitative yield of the corresponding acyloxytrichlorosilanes. The latter were colorless, mobile liquids, which fumed in air and on more or less prolonged standing disporportionated into tetraacyloxysilanes and silicon tetrachloride:

$$4RCOOSiCl_3 \longrightarrow (RCOO)_4Si + 3SiCl_4 \qquad (1)$$

The tendency for disproportionation increased with increasing strength of the organic acid, forming part of the acyloxytrichlorosilane, as is shown by the data presented in Table 1 on the rates of disproportionation of various acyloxytrichlorosilanes.

TABLE 1

Rate of Disproportionation of Acyloxytrichlorosilanes

Acid, forming acyloxytrichlorosilane	p-Toluic	Benzoic	p-Chlorobenzoic	o-Toluic	m-Nitrobenzoic	p-Nitrobenzoic	o-Chlorobenzoic	o-Nitrobenzoic
$k \cdot 10^5$	4.33	6.46	10.4	12.2	34.0	39.8	120	695
Time for the beginning of disproportionation of acyloxytrichlorosilanes*	3 days	—	2 hrs.	6 hrs.	1 hr.	1 hr.	30 min.	30 min.
Time for complete disproportionation	60 days	30 days	4 hrs	1 hr.	2 hrs.	2 hrs.	1 hr.	1 hr.

* Time to the appearance of the first crystals of silicoanhydride.

The acyloxytrichlorosilanes may be stored for a longer time by dilution with inert solvents (benzene and ether).

After vacuum distillation, the acyloxytrichlorosilanes keep longer since even minute amounts of free acid in the undistilled materials promote more rapid disproportionation. This was established on the example of benzoyloxytrichlorosilane and explains the more rapid decomposition of p-chlorobenzoyloxytrichlorosilane, which could not be distilled, in comparison with the decomposition of o-toluyloxytrichlorosilane, purified by distillation.

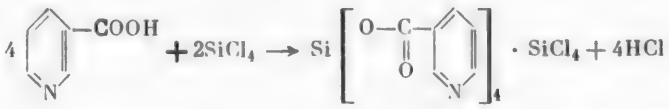
However, it is also necessary to consider the solubility of silicoanhydrides both in acyloxytrichlorosilanes and in silicon tetrachloride: silicobenzoic anhydride is noticeably soluble in benzoyloxytrichlorosilane and in silicon tetrachloride and therefore the separation of its crystals was not observed for a long time.

Raising the temperature accelerated disproportionation and due to this the acyloxytrichlorosilanes partially decomposed during vacuum distillation. Some acyloxytrichlorosilanes, such as α-naphthoyloxytrichlorosilane and chloro- and nitrobenzoyloxytrichlorosilanes, for example, decomposed completely on vacuum distillation. Therefore, in distilling off the excess silicon tetrachloride, the bulk of it had to be removed on a warm (50 – 55°) water bath at 100 – 200 mm Hg and the rest in high vacuum after preliminary removal of the water bath so as to prevent partial disproportionation of the acyloxytrichlorosilane. Prolonged vacuum treatment also promoted disproportionation of acyloxytrichlorosilanes, but to a considerably lesser extent than an elevated temperature. Acyloxytrichlorosilanes had to be distilled as rapidly as possible at a low residual pressure, since otherwise their decomposition was increased: in a distillation of benzoyloxytrichlorosilane at 400 mm, we obtained only benzoyl chloride (62%) and benzoic anhydride (32%), formed as a result of further conversions of the disproportionation products, silicobenzoic anhydride and silicon tetrachloride (see below).

We should also note that the solubility of the acids in silicon tetrachloride was of great importance in the synthesis of acyloxytrichlorosilanes: due to the low solubility of o-chlorobenzoic acid, extremely long heating was required for the preparation of o-chlorobenzoyloxytrichlorosilane; p-chloro- and o- and p-nitrobenzoic acids are practically insoluble and therefore, under normal conditions, they formed only the corresponding tetraacyloxysilanes, which are also insoluble.

p-Chlorobenzoyloxytrichlorosilane could only be obtained by carrying out the reaction in a mixture (1 : 1) of silicon tetrachloride and ether, in which the acids are readily soluble. and p-Nitrobenzoyloxytrichlorosilanes could be obtained by carrying out the reaction in a mixture (1 : 1) of silicon tetrachloride and acetone, in which the starting acids are readily soluble. Under the conditions described, silicon tetrachloride did not react with ether or acetone and the use of the latter to improve the solution of the acids considerably increased the rate of formation of acyloxytrichlorosilanes, for example, by a factor of 10 in the formation of o-chlorobenzoyloxytrichlorosilane.

In the reaction of nicotinic acid with silicon tetrachloride, we obtained only a complex of siliconicotinic anhydride with one molecule of silicon tetrachloride, since nicotinic acid is insoluble in silicon tetrachloride, ether, acetone and certain other inert solvents.



(2)

We studied the formation mechanism of acyloxytrichlorosilanes as an example of the interaction of silicon tetrachloride with o-chlorobenzoic and with benzoic acid.

When o-chlorobenzoic acid was boiled for 20 minutes in a mixture (1 : 1) of silicon tetrachloride and ether, we isolated only unchanged acid (92%); after 1 hour's boiling, we obtained o-chlorobenxoyloxytrichlorosilane (40%) and unchanged acid (52%); after 2 hour's boiling, o-chlorobenzoyloxytrichlorosilane was obtained in almost quantitative yield.

When benzoic acid was boiled for 20 minutes in excess silicon tetrachloride, unchanged acid (88%) was isolated; after 1 hour's boiling, benzoyloxytrichlorosilane (35%) and unchanged acid (54%) were obtained; after 2.5 hour's boiling, benzoyloxytrichlorosilane was obtained in almost quantitative yield (with an insignificant amount of the original acid).

TABLE 2

Acyloxytrichlorosilanes

Name of acyl group	% Si		%Cl (hydrolyzable)		Yield (after distillation) and boiling point
	found	calc.	found	calc.	
o-Toluyl-	10.18, 10.35	10.41	39.53, 39.56	39.48	81%; b.p. 109—110° (6 mm)
p-Toluyl-	10.21, 10.27	10.41	39.62, 39.77	39.48	73%; b.p. 115—116° (6 mm)
o-Chlorobenzoyl-	9.43, 9.47	9.69	36.92, 36.97	36.69	Undistillable
p-Chlorobenzoyl-•	9.34, 9.38	9.69	37.07, 37.15	36.69	» »
o-Nitrobenzoyl-	9.05, 9.11	9.34	35.69, 35.72	35.40	» »
m-Nitrobenzoyl-	8.98, 9.02	9.34	35.61, 35.68	35.40	» »
p-Nitrobenzoyl-••	9.02, 9.12	9.34	35.63, 35.67	35.40	» »
α-Naphthoyl-	8.95, 9.01	9.19	35.02, 35.09	34.82	» »
α-Furoyl-	11.37, 11.38	11.42	43.23, 43.38	43.35	67%; b.p. 93—94° (8 mm)
α-Thenoyl-	10.57, 10.62	10.74	40.41, 40.54	40.66	85%; b.p. 95—96° (5 mm)

• The reaction was carried out in a mixture of absolute ether and silicon tetrachloride (1 : 1) for 5 hours.

•• The reaction was carried out in a mixture of absolute acetone and silicon tetrachloride (1 : 1) for 5 hours.

TABLE 3

Disproportionation Products of Acyloxytrichlorosilanes

Name of acyl group	Am't (in g)	Standing time	Disproportionation products				
			$SiCl_4$ (yield in %)	silicoanhydride			
				name	yield (in %)	%Si	
						found	calc.
p-Touyl-	5.4	60 days	70	Silico-p-toluic	88	4.72, 4.77	4.93
Benzoyl•	5.1	30 days	90	Silicobenzoic	98	5.32, 5.39	5.48
o-Toluyl-	16.5	24 hrs.	66	Silico-o-toluic	85	4.97, 5.15	4.93
p-Chlorobenzoyl-	5.8	4 hrs.	74	Silico-p-chlorobenzoic	93	4.51, 4.55	4.32
m-Nitrobenzoyl-	6.0	2 hrs.	71	Silico-m-nitrobenzoic	93	4.22, 4.28	4.05
p-Nitrobenzoyl-	6.0	2 hrs.	78	Silico-p-nitrobenzoic	89	4.29, 4.36	4.05
o-Chlorobenzoyl-	5.8	1 hr.	75	Silico-o-chlorobenzoic	93	4.55, 4.60	4.32
o-Nitrobenzoyl-	6.0	1 hr.	76	Silico-o-nitrobenzoic	86	4.31, 4.36	4.05
α-Thenoyl-	5.8	10 days	85	Silicoanhydride of α-thiophenecarboxylic acid	95	5.05, 5.11	5.23

• The silicon tetrachloride was sucked off in vacuum through a tube with alkali and determined by the gain in weight.

Thus, the action of excess silicon tetrachloride on an organic acid forms an acyloxytrichlorosilane without the formation of any intermediate compounds.

$$RCOOH + SiCl_4 \longrightarrow RCOOSiCl_3 + HCl \quad (3)$$

$R = C_6H_5$; o-, p-$CH_3C_6H_4$; o-, p-ClC_6H_4, o-, m-, p-$NO_2C_6H_4$, $C_{10}H_7$, C_4H_3O, C_4H_3S.

In studying the properties of the acyloxytrichlorosilanes obtained, we examined their decomposition reactions under various conditions. On the example of benzoyloxytrichlorosilane, we established that the most extensive decomposition of it occurred when it was distilled at atmospheric pressure and led to the formation of benzoyl chloride, silicon dioxide and silicon tetrachloride [1].

$$2C_6H_5COOSiCl_3 \longrightarrow 2C_6H_5COCl + SiO_2 + SiCl_4 \quad (4)$$

However, this equation represents only the initial and final states of the system under the most drastic conditions and reflects none of the intermediate processes occuring. The experimental data we obtained form a basis for the following scheme for the thermal decomposition of benzoyloxytrichlorosilane.

1. Benzoyloxytrichlorosilane disproportionates into the silicoanhydride and silicon tetrachloride, which, as was indicated above, occurs under milder conditions, namely, vacuum distillation and standing:

$$4C_6H_5COOSiCl_3 \longrightarrow (C_6H_5COO)_4Si + 3SiCl_4 \quad (5)$$

2. Silicobenzoic anhydride decomposes further into benzoic anhydride and silicon dioxide;

$$(C_6H_5COO)_4Si \longrightarrow 2(C_6H_5CO)_2O + SiO_2 \quad (6)$$

3. The benzoic anhydride formed reacts with silicon tetrachloride on the one hand and benzoyloxytrichlorosilane on the other to give benzoyl chloride and silicon dioxide:

$$2(C_6H_5CO)_2O + SiCl_4 \longrightarrow 4C_6H_5COCl + SiO_2 \quad (7)$$

$$(C_6H_5CO)_2O + C_6H_5COOSiCl_3 \longrightarrow 3C_6H_5COCl + SiO_2 \quad (8)$$

Cases are known in the literature [2 – 4] of the thermal decomposition of silicoanhydrides of aliphatic acids with the formation of anhydrides and silicon dioxide. We vacuum distilled silicobenzoic anhydride and obtained benzoic anhydride in 85% yield.

The formation of acetyl chloride and silicoacetic anhydride from acetic anhydride and silicon tetrachloride has already been described by Friedel and Ladenburg [2] and is a preparative method for obtaining silicoacetic anhydride [5]. Taurke [6] has reported the formation of benzoyl chloride from silicon tetrachloride and benzoic anhydride.

We reacted silicon tetrachloride with benzoic anhydride and found that with vacuum distillation of the products, the benzoyl chloride yield was 74%; with a normal distillation, the yield was 80%, confirming the accuracy of equation (7).

By vacuum distillation of a mixture (1 : 1) of benzoic anhydride and benzoyloxytrichlorosilane, we obtained benzoyl chloride in 64% yield and unchanged benzoic anhydride (26%); with a normal distillation, the yields were 74% and (18%), respectively, which confirms the accuracy of equation (8).

All the data presented above substantiate the scheme we have put forward for the thermal conversion of benzoyloxytrichlorosilane into benzoyl chloride.

EXPERIMENTAL

Preparation of Acyloxytrichlorosilanes

The acyloxytrichlorosilanes, obtained in the present work in quantitative yield (before distillation) by the procedure described previously [1], are presented in Table 2. The course of the reaction was studied on the example of the preparation of benzoyloxy- and o-chlorobenzoyloxytrichlorosilane.

Preparation of benzoyloxytrichlorosilane. a) A mixture of 12.2 g (0.1 mole) of benzoic acid and 30 ml (0.26 mole) of silicon tetrachloride was boiled for 2.5 hours (during this time an equimolar amount of hydrogen chloride was liberated); 25 g (98%) of benzoyloxytrichlorosilane with small tracesof the original acid was obtained.

Found %: Si 10.39, 10.43; Cl 40.88, 40.82. $C_7H_5O_2Cl_3Si$. Calculated %: Si 10.98; Cl 41.65.

b) When the same mixture of reagents was boiled for 1 hour, the yield of benzoyloxytrichlorosilane fell

to 35% (Found %: Si 10.46, 10.55; Cl 40.89, 40.96), and 6.6 g (54%) of unchanged benzoic acid with m.p. 121.5 – 122° was isolated; a mixed melting point with authentic benzoic acid was not depressed.

c) When the mixture was boiled for 20 minutes, only benzoic acid (10.7 g, 88%) was isolated.

Preparation of o-chlorobenzoyloxytrichlorosilane. a) When a mixture of 2.5 g (0.016 mole) of o-chlorobenzoic acid, 20 ml (0.16 mole) of silicon tetrachloride and 20 ml of absolute ether was boiled for 2 hours, we isolated 4.5 g (98%) of o-chlorobenzoyloxytrichlorosilane.

Found %: Si 9.40, 9.46; $Cl_{hyd.}$ 36.95, 37.00. $C_7H_4O_2Cl_4Si$. Calculated %: Si 9.69; $Cl_{hyd.}$ 36.69.

b) When a similar mixture of reagents was boiled for 1 hour, the yield of o-chlorobenzoyloxytrichlorosilane was 40% (Found %: Si 9.41, 9.48; $Cl_{hyd.}$ 36.89, 36.98) and together with this, we isolated 1.3 g (52%) of unchanged o-chlorobenzoic acid with m.p. 140°; a mixed melting point with authentic o-chlorobenzoic acid was not depressed.

c) With 20 minutes' boiling, only unchanged o-chlorobenzoic acid (2.3 g, 92%) was isolated.

Disproportionation of Acyloxytrichlorosilanes

Freshly prepared acyloxytrichlorosilane was placed in a closed test tube and the time required for separation of the first crystals of tetraacyloxysilane noted. When the separation of crystals obviously ceased, the liquid was decanted from the precipitate and distilled. The crystals were washed with absolute ether and analyzed.

The results obtained are presented in Table 3.

The preparation of tetraacyloxysilanes was achieved by the procedure described for the synthesis of acyloxytrichlorosilanes [1]. Table 4 gives the silicoanhydrides we obtained and they appeared as white, powdery substances, which decomposed without melting above 300° (they are not described in the literature).

TABLE 4

Tetraacyloxysilanes

Name of acyl group	%Si		%Cl	
	found	calc.	found	calc.
p-Chlorobenzoyl-	4.43, 4.47	4.32	—	—
o-Nitrobenzoyl-	4.14, 4.19	4.05	—	—
p-Nitrobenzoyl-	3.96, 4.35	4.05	—	—
Nicotinoyl- (complex of silicoanhydride with one molecule of $SiCl_4$)	8.24, 8.28	8.18	20.79, 20.84	20.66

The Mechanism of The Thermal Conversion of Benzoyloxytrichlorosilane Into Benzoyl Chloride

Benzoic anhydride from silicobenzoic anhydride. Dry silicobenzoic anhydride, obtained by the method of K. D. Petrov and E. S. Lagucheva [7] from 12.2 g (0.1 mole) of benzoic acid and 5.1 g (0.03 mole) of silicon tetrachloride in 100 ml of absolute benzene, was vacuum distilled. We obtained 9.6 g (85%) of a distillate, which was benzoic anhydride: the b.p. was 173 – 175° (2 mm) and the m.p. 39.5 – 40°. A mixed melting point with authentic benzoic anhydride was not depressed.

Benzoyl chloride from benzoic anhydride. a) A mixture of 7.5 g (0.033 mole) of benzoic anhydride and 3.0 g (0.018 mole) of silicon tetrachloride was heated for 30 minutes on a water bath at 60 – 70° and vacuum distilled at 15 mm. We obtained 6.9 g (74%) of benzoyl chloride, b.p. 93 – 94° (15 mm), n_D^{20} 1.5536, d_4^{20} 1.2127 and 1.2 g (16%) of unchanged benzoic anhydride with b.p. 205 – 207° (15 mm) and m.p. 39 – 39.5°. Literature data for benzoyl chloride: b.p. 193.9 – 194.1°, n_D^{20} 1.55369, d_4^{20} 1.2122 [8].

In a similar experiment with the reaction product distilled at 738 mm, we obtained 7.5 g (80%) of benzoyl chloride with b.p. 193 – 194° (738 mm), n_D^{20} 1.5535 and 0.8 g (11%) of unchanged benzoic anhydride with b.p. 204 — 206° (14 mm) and m.p. 39.5 – 40°.

b) A mixture of 4.52 g (0.02 mole) of benzoic anhydride and 5.1 g (0.02 mole) of benzoyloxytrichlorosilane was vacuum distilled at 40 mm. We obtained 5.4 g (64%) of benzoyl chloride with b.p. 102 – 103° (40 mm), n_D^{20} 1.5534 and 1.8 g (26%) of unchanged benzoic anhydride with b.p. 220 – 222° (40 mm) and m.p. 39 – 39.5°.

Distillation of the same mixture of reagents at 740 mm yielded 6.2 g (74%) of benzoyl chloride with b.p. 194 – 195° (740 mm), n_D^{20} 1.5536 and 1.2 g (18%) of unchanged benzoic anhydride with b.p. 202 – 204° (12 mm) and m.p. 39.5 – 40°.

SUMMARY

1. Aroyloxytrichlorosilanes and also furoyloxy- and thenoyloxytrichlorosilanes were obtained in quantitative yields by heating appropriate acids with excess silicon tetrachloride.

2. The acyloxytrichlorosilanes were relatively readily disproportionated into the corresponding silicoanhydrides and silicon tetrachloride. The tendency for disproportionation increased with an increase in the strength of the organic acid, forming part of the acyloxytrichlorosilane. An increase in temperature, a trace of the original acid and also a reduction in pressure promoted disproportionation.

3. The formation of acyloxytrichlorosilanes proceeded only in solution: organic acids, which were insoluble in silicon tetrachloride, formed only tetraacyloxysilanes. To prepare acyloxytrichlorosilanes from such acids it was necessary to add suitable solvents (ether and acetone).

4. On the example of benzoyloxytrichlorosilane, a scheme is presented for the mechanism of the thermal conversion of an acyloxytrichlorosilane into the acid halide of the corresponding acid.

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A CONTRIBUTION ON THE REDUCTION OF NITRO DERIVATIVES OF DIPHENYLMETHANE WITH ALKALI SULFIDES

L. M. Litvinenko, N. F. Levchenko, S. V. Tsukerman and R. S. Cheshko

Kharkhov State University

In connection with our work [1 – 10] on the partial sodium sulfide reduction of dinuclear aromatic dinitro derivatives, in which the nitro groups are in different bezene rings, a need arose for investigating the action of alkali sulfides on 4, 4'-dinitrodiphenylmethane. This problem was recently touched on in the dissertation of R. S. Tsekhanskii [11], where it was shown that treatment of 4, 4'-dinitrodiphenylmethane with sodium hydrosulfide in an alcohol-water medium yielded 4-amino-4'-nitrodiphenylmethane, melting at 246°. However, as a result of many repeats of R. S. Tsekhanskii's experiments, we convinced ourselves that here, besides a compound with m.p. 246° (subsequently called substance I), commensurable amounts of another substance with m.p. 178° (substance II) were formed and this was quite readily separated from the first one due to its lower solubility in alcohol.

A preliminary examination of the physical properties of substance (I) showed that it was not 4-amino-4'--nitrodiphenylmethane. Thus, in contrast to most nitroamines of analogous structure, it was extremely difficultly soluble in benzene, while, on the other hand, its hydrochloride dissolved very readily in aqueous hydrochloric acid. The melting point of this product was too high for a compound with such an unsymmetrical structure as 4-amino-4'-nitrodiphenylmethane. Chemical methods of investigation showed that substance (I) did not in fact have the structure of this nitroamine. For example, attempts to convert it into the known 4, 4'-diaminodiphenylmethane [12] with hydrazine hydrate in the presence of Raney nickel [13] (cf. [2 – 6, 8, 14]) always ended with isolation of the starting product. In a potentiometric titration of substance (I) (assuming that its molecular weight was approximately the same as that of 4-amino-4'-nitrodiphenylmethane) with sodium nitrite in a hydrochloric acid medium [15], it was found that the nitrite consumed was almost equivalent to two amino groups. If substance (I) was dissolved in dichloroethane and a stream of dry hydrogen chloride passed through the solution, then an amine hydrochloride was precipitated, which contained 2 moles of HCl in its composition. Finally, if to substance (I) in dichloroethane solution was added excess (approximately 3 times the molecular ratio) of benzoyl chloride or p-nitrobenzoyl chloride in the same solvent and then when the reaction was complete, the unreacted acid chloride was determined quantitatively [16, 17], it was found that the acylation consumed 2 moles of acid chloride.

All that has been said above shows that substance (I) was a diamine. The most simple assumption is that it was the product from reduction of both nitro groups in 4, 4'-dinitrodiphenylmethane, i.e. 4, 4'-diaminodiphenylmethane, but this is immediately rejected since the latter compound melts almost 150° lower (93° [12]). For elucidating the structure of substance (I), the report on the possibility of converting 4, 4'-diaminodiphenylmethane into 4, 4'-diaminobenzophenone (m.p. 244° [19]) by treatment with alkali sulfides [18] was of great importance. This conversion may be explained by the fact that in the action of sulfur compounds on 4, 4'-diaminodiphenylmethane, as in the case of the reaction of diphenylmethane itself with sulfur [20], a thioketone is first formed and this is then readily hydrolyzed into a benzophenone derivative. Therefore, we may assume that in the interaction of an alkali sulfide with 4, 4'-dinitrodiphenylmethane there are two processes, namely, reduction of the nitro groups into amino groups and conversion of the methylene grouping into a carbonyl. Actually, substance (I) was found to be identical with an authentic sample of 4, 4'-diaminobenzophenone, obtained by a procedure described in the literature [21].

We found that 4, 4'-diaminobenzophenone was obtained much more smoothly and in good yield by treating 4, 4'-dinitrodiphenylmethane with sodium disulfide in aqueous methanol. The latter procedure may be used as a new and convenient method of synthesizing this diamine.

After establishing the structure of substance (I), it was not difficult to prove the structure of substance (II). Potentiometric titration of it with nitrite showed that it was a monoamine. In melting point and other properties, it was identical with 4-amino-4'-nitrobenzophenone, which is formed by hydrolysis of the p-nitrobenzoyl derivative of N-phenylphthalimide [22]. Finally, the structure of substance (II) was demonstrated by its reduction with hydrazine hydrate in the presence of Raney nickel to give 4, 4'-diaminobenzophenone.

It is interesting to note that even under more drastic conditions than in the reduction of 4, 4'-dinitrodiphenylmethane with sodium disulfide, the action of the same reagent on 4-nitrodiphenylmethane led to the formation of only 4-aminodiphenylmethane, i.e. the conversion of the methylene group into a carbonyl did not occur to a noticeable extent here.

EXPERIMENTAL

1. Synthesis of 4, 4'-dinitrodiphenylmethane. We introduced some changes and refinements into the procedure for synthesizing this compound described by Staedel [23] and this made it possible to obtain completely reproducible results. With stirring, 10 g of finely powdered diphenylmethane was introduced in small portions into 60 g concentrated nitric acid (d 1.51), which was first cooled to -10°. The temperature in the mixture was not allowed to rise above 0°. This operation usually took 10 – 15 minutes. The solution formed, together with the crystalline product liberated, was then carefully poured into 600 – 800 ml of ice-water with very vigorous stirring. The crystalline substance was washed with water, first by decantation and then on a vacuum funnel. The product was carefully ground with methyl alcohol as a liquid paste, pressed out well and treated with boiling ether several times to extract impurities until the last portions of ether did not acquire a yellow color. The almost colorless crystalline product was recrystallized from benzene twice. The mp. was 183 – 185°. The yield was 6.5 g (42.3%).

2. Action of sodium hydrosulfide on 4, 4'-dinitrodiphenylmethane.* A solution of sodium hydrosulfide (16 ml)** was added dropwise to a suspension of 5 g of 4, 4'-dinitrodiphenylmethane in 300 ml of alcohol, heated to boiling, and the misture boiled under reflux for 3 hours.*** On cooling, the solution deposited a light brown crystalline precipitate.

a) Isolation of substance (I). The precipitate indicated above was removed from the solution, which was then evaporated as far as possible. The reaction product was extracted from the residual tarry mass with several portions of dilute (1 : 1) hydrochloric acid with boiling. The combined extracts were treated with activated charcoal and the amino derivative precipitated by the gradual addition of ammonia. The yield was 0.7 g. This substance was recrystallized once from ethyl alcohol and then dissolved in dichloroethane (activated charcoal) and precipitated in the form of the hydrochloride by passing dry hydrogen chloride into the solution. The latter operation was repeated at least once more. The hydrochloride was recrystallized several times (at first with activated charcoal) from hydrochloric acid (1 : 1). After decomposition of the hydrochloride with aqueous ammonia, the amine was recrystallized many times from dilute methyl alcohol (2 : 1) to a constant melting point of 246°. A mixed melting point of this substance with a sample of 4, 4'-diaminobenzophenone, prepared by a method described in the literature [21], was not depressed.

Found %: NH_2 [15], 15.0, 15.1. $C_{13}H_{12}ON_2$. Calculated %: NH_2 15.1

Hydrochloride of 4, 4'-Diaminobenzophenone

Found %: Cl 24.8, 24.5. $C_{13}H_{14}ON_2Cl_2$. Calculated %: Cl 24.9

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* In this experiment we followed the procedure of R. S. Tsekhanskii [11]; we isolated the reaction products differently.

** A stream of hydrogen sulfide was passed for 5 – 6 hours through 150 ml of an aqueous solution of sodium sulfide, prepared from 34 g of $Na_2S \cdot 9H_2O$. A solution obtained in this way could be used immediately or after several days.

*** It was noted that identical results were obtained by either gradual or by single addition of the hydrosulfide and also with changes in the heating time of the mixture over the range of 2 - 3 hours.

Substance (I) yielded a benzylidene derivative with m.p. 194°, identical with the compound formed by heating authentic 4, 4'-diaminobenzophenone with benzaldehyde [21].

b) Isolation of substance (II). The light brown precipitate, separated from the mother solution, was treated with several portions of boiling dilute (1 : 1) hydrochloric acid. The reaction product was precipitated from the combined extracts (activated charcoal) with ammonia. The yield was 0.5 g. The substance was recrystallized many times from alcohol (at first with activated charcoal) to a constant melting point equal to 178° (according to data in [22], 4-amino-4'-nitrobenzophenone has m.p. 176.5–177.5°).

Found %: NH_2 [15] 6.50, 6.59. $C_{13}H_{10}O_3N_2$. Calculated %: NH_2 6.61

The yellow substance with an orange tinge was insoluble in water, but readily soluble in the usual organic solvents.

3. Conversion of substance (II) into 4, 4'-diaminobenzophenone. Raney nickel was gradually introduced in small portions into a solution of 0.2 g of substance (II) in 10 ml of warm methyl alcohol, containing 0.2 ml of 98% hydrazine hydrate, with the observation of all the special procedures, described in detail previously [4, 13, 14]. After completion of the reaction (the evolution of nitrogen ceased), the liquid was filtered free from catalyst and evaporated to small volume. The precipitated crystalline substance was recrystallized several times from dilute (2 : 1) methyl alcohol. The m.p. was 244°. A mixed melting point with an anthentic sample of 4, 4'-diaminobenzophenone [21] was not depressed.

4. Action of sodium disulfide on 4, 4'-dinitrodiphenylmethane. Over a period of 15 minutes, 80 ml of a molar solution of sodium disulfide* was added to a boiling solution of 6.6 g of 4, 4'-dinitrodiphenylmethane in 800 ml of methyl alcohol and then boiling under reflux was continued for another hour. The mixture was acidified with concentrated hydrochloric acid and the solvent almost completely evaporated. The residue was treated several times with boiling dilute (1 : 1) hydrochloric acid. The combined extracts (activated charcoal) were evaporated to small volume and on cooling, they deposited crystals of 4, 4'-diaminobenzophenone hydrochloride. The yield was 6.6 g (90.5%). This product was then purified as indicated in the isolation of substance (I). The m.p. was 246°. A mixed melting point with an authentic sample of 4, 4'-diaminobenzophenone [21] was not depressed.

5. Action of sodium disulfide on 4-nitrodiphenylmethane. 500 ml of a molar solution of sodium disulfide** was added to a solution of 21 g of 4-nitrodiphenylmethane (see [23], p. 160) in 240 ml of boiling methyl alcohol and the mixture boiled for 3 hours. The solvent was evaporated and the amine extracted from the residue with ether. The ether solution was dried with anhydrous sodium sulfate, treated with charcoal and the solvent evaporated. To the oily residue was added concentrated hydrochloric acid and the crystals formed were recrystallized twice from dilute (1 : 1) hydrochloric acid. The yield was 8.7 g (49%). The salt was decomposed with warm aqueous ammonia and the product, which crystallized on cooling, was recrystallized several times from dilute (2 : 1) methyl alcohol. The m.p. was 35°, which corresponds with [24].

SUMMARY

The action of sodium hydrosulfide in aqueous alcohol on 4, 4'-dinitrodiphenylmethane caused conversion of the methylene group into a carbonyl in addition to reduction of the nitro groups and a mixture of 4, 4'-diaminobenzophenone and 4-amino-4'-nitrobenzophenone was formed. Similarly, treatment of 4, 4'-dinitrodiphenylmethane with sodium disulfide in aqueous methyl alcohol yielded 4, 4'-diaminobenzophenone. The reduction of 4-nitrodiphenylmethane with sodium disulfide in aqueous methanol was not accompanied by a change in the methylene group and led to the formation of 4-aminodiphenylmethane.

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* The solution was prepared in the following way: 240 g of $Na_2S \cdot 9H_2O$ and 32 g of sulfur were heated in 500 ml of water and 250 ml of methyl alcohol until solution was complete and the cooled solution was diluted to 1 liter with water.

** Refers to previous footnote

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PREPARATION OF PHOSPHORUS DIIODIDE AND TRIIODIDE

É. S. Levchenko, I. E. Sheinkman and A. V. Kirsanov

Institute of Organic Chemistry, Academy of Sciences, Ukranian SSR

Up to now, phosphorus diiodide has not been used as the starting material for the synthesis of organophosphorus compounds. There is only one paper in which it was reported that phosphorus diiodide reacted with alkyl halides [1]. Unfortunately, there is no description of the experiments, the yields, the properties and the analyses of the substances obtained. Phosphorus diiodide must be an extremely reactive substance and may be used as the starting material for the synthesis of various organophosphorus compounds; therefore, a detailed study of the chemical properties of phosphorus diiodide is of great theoretical and practical interest.

Up to now phosphorus diiodide has not been used for preparative purposes only because its preparation in a pure state involves great difficulty. Handbooks on preparative inorganic chemistry [2] present the method of Germann and Traxler [3] as the best one and this is based on the reaction of pure iodine with white phosphorus in carefully purified carbon disulfide. The method is inconvenient, dangerous for the preparation of large amounts of phosphorus diiodide and requires the use of very pure starting materials, since the final product is not recrystallized and therefore includes all the impurities present in the starting materials.

The problem of this investigation was the development of a safe and comparatively convenient method of preparing phosphorus diiodide and in passing, to develop a method of preparing and purifying phosphorus triiodide without the use of white phosphorus and carbon disulfide.

According to literature data, pure phosphorus diiodide has m.p. 124.5°, which does not correspond with reality. Quite pure phosphorus diiodide melts at 126 – 127° (see below).

Phosphorus diiodide was first prepared by Gay-Lussac in 1813 [4] and then by Wurtz [4] by fusion of 1 part of red phosphorus with 8 – 10 parts of iodine [4]. The product obtained by this method had m.p. 100°. Doughtly [4] obtained phosphorus diiodide with m.p. 110° by heating a mixture of 50 g of iodine with 4 g of red phosphorus over a burner until it melted, cooling the melt to 60° and then adding 2.5 g of white phosphorus in small portions.

Corenwinder [4] obtained phosphorus diiodide by reacting 2 g-at of iodine with 1 g-at of white phosphorus in carbon disulfide solution. With slight changes, this method was used for the preparation of phosphorus diiodide by many other authors [4]. The melting point of the product obtained by this method did not exceed 110°.

Using this method, but working with very pure carbon disulfide, Germann and Traxler [3] obtained phosphorus diiodide with m.p. 124.5°. The authors showed that the phosphorus diiodide obtained in normal carbon disulfide was contaminated by side products formed due to sulfur and other impurities present in the carbon disulfide.

By the reduction of phosphorus triiodide with white phosphorus in carbon disulfide, V. Ginzburg and N. Privezentseva [5] obtained phosphorus diiodide with m.p. 124°. In addition, a series of reactions were described for the preparation of phosphorus diiodide, but these cannot be used at present as the basis of a preparative method [4].

Thus, according to methods described in the literature, it is only possible to obtain comparatively pure phosphorus diiodide by the use of white phosphorus in carbon disulfide.

Hautefeuille showed that the reaction of hydrogen iodide with phosphorus trichloride gave phosphorus triiodide and Besson carried out this reaction in carbon tetrachloride solution and obtained pure phosphorus triiodide with m.p. 61° [4]. This method is inconvenient for preparative purposes.

Corenwinder and other authors [4] obtained phosphorus triiodide with m.p. 55° by the action of 3 g-at of iodine on 1 g-at of white phosphorus in carbon disulfide solution. Besson showed that phosphorus triiodide could not be obtained in a pure state by Corenwinder's method, since the solubility of phosphorus triiodide in carbon disulfide is very great and for the isolation of phosphorus triiodide it is necessary to evaporate to very high concentrations, at which impurities precipitate from the solution. Germann and Traxler used the data of Corenwinder and Besson and by the use of very pure starting materials and specially purified carbon disulfide, they obtained phosphorus triiodide with m.p. 61° by Corenwinder's method. They also showed that phosphorus triiodide could be obtained in carbon disulfide solution from iodine and very pure red phosphorus [3]. Up to the present time, the procedure of Germann and Traxler was the most convenient and therefore is presented in most handbooks on preparative inorganic chemistry [2]. Other reactions by which phosphorus triiodide is formed, could not be used preparatively.

Thus, for the preparation of pure phosphorus triiodide, it is also impossible to avoid the use of carbon disulfide and therefore the preparation of large amounts of phosphorus triiodide for preparative purposes involves difficulties.

After many experiments it was found that phosphorus diiodide and triiodide could be prepared in a completely pure state directly from iodine and red phosphorus with subsequent recrystallization from suitable solvents. The reaction could be carried out by preliminary fusion of the iodine and phosphorus or by boiling iodine and phosphorus in the solvent used for recrystallization.

For the recrystallization of phosphorus diiodide it is possible to use butyl iodide and bromide, dichloroethane, ethyl iodide and other alkyl and alkene halides, but the most suitable solvent is chlorobenzene. The phosphorus diiodide obtained in this way appeared as coarse, long orange plates with m.p. 126 – 127°. There were no difficulties involved in the preparation of comparatively large amounts of the material. Under laboratory conditions, in a working day a chemist can readily prepare 1 kg of pure phosphorus diiodide.

For the recrystallization of phosphorus triiodide, it is possible to use carbon tetrachloride, chloroform and butyl iodide, but best of all is dichloroethane. Phosphorus triiodide was thus obtained in the form of coarse, lustrous, dark red crystals with m.p. 60 – 61°.

EXPERIMENTAL

"Pure" grade iodine was used without further purification. The red phosphorus was washed with hot water and alcohol and dried in a vacuum desiccator. The solvents used were dried carefully.

Preparation of phosphorus diiodide. A. One g-at of powdered iodine was mixed with 0.75 g-at of red phosphorus (50% excess) in a flask, protected from atmospheric moisture with a calcium chloride tube. If the reaction did not begin spontaneously, then the mixture was carefully heated over a small flame. When the evolution of heat had ceased, the melt was heated on an oil bath at 180 – 190° (oil temperature) for 1 hour with continuous stirring. With longer heating or with a higher temperature, the final product had a lower melting point. On cooling, the melt was dissolved in 180 ml of boiling chlorobenzene and the solution filtered. After cooling, the filtrate deposited phosphorus diiodide in the form of coarse long orange plates. The product was sucked dry, washed with hot chloroform (80 ml), which did not contain alcohol, and dried in vacuum. Hot carbon tetrachloride or dichloroethane could also be used for washing. The yield was about 70% and the m.p. 121 – 123°. After a second recrystallization from 275 ml of chlorobenzene with subsequent washing with hot chloroform (80 ml), the yield was about 40% and the m.p. 126 – 127°.

B. Red phosphorus was added in small portions with stirring to 6 N iodine solution in butyl iodide, allowing 0.6 g-at of phosphorus to 1 g-at of iodine (20% excess). Heat was evolved when the red phosphorus was added. The reaction mixture was then boiled under reflux for 3 hours with continuous stirring. The hot solution was filtered to remove excess phosphorus. On cooling, the solution deposited phosphorus diiodide, which was sucked dry, washed with carbon tetrachloride and dried in vacuum. The yield was about 40% and the m.p. 124 – 126° (after a second recrystallization from butyl iodide, the product had m.p. 126 – 127°).

C. A mixture of 0.1 mole of phosphorus triiodide, 0.075 g-at of red phosphorus (50% excess) and 45 ml of butyl iodide was boiled under reflux for 2 hours, the excess phosphorus removed by filtration and the crystals of phosphorus diiodide, which separated on cooling, were sucked dry, washed with carbon tetrachloride and dried in vacuum. The yield was about 60% and the m.p. 126 – 127°.

Preparation of phosphorus triiodide. A. Two g-at of powdered iodine and 0.67 g-at of red phosphorus were mixed in a flask, protected from atmospheric moisture with a calcium chloride tube. An exothermic reaction began and the mixture was converted into a homogeneous dark melt (if the reaction did not begin spontaneously, the mixture was carefully heated over a flame until the reaction began). The cooled solid mass was dissolved in 500 ml of boiling dichloroethane and the solution filtered. The solution was cooled slowly (so that the product did not precipitate as an oil) and the coarse, dark red prismatic crystals of phosphorus triiodide which separated were sucked dry, washed with carbon tetrachloride (3 x 20 ml) and dried in vacuum. The yield was about 65% and the m.p. 60 – – 61°.

B. Red phosphorus was added to a 2.5 N solution of iodine in dichloroethane, allowing 1.02 g-at of phosphorus to 3 g-at of iodine, and the mixture boiled under reflux for 15 minutes. The hot solution was filtered and the phosphorus triiodide, which precipitated on cooling, was sucked dry, washed with carbon tetrachloride and dried in vacuum. The yield was about 55% and the m.p. 60 – 61°.

SUMMARY

Preparative methods were developed for the preparation of phosphorus diiodide and triiodide without the use of white phosphorus and carbon disulfide.

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ORGANOBORON COMPOUNDS

XXXVI. SYNTHESIS OF HEXASUBSTITUTED BORAZOLE FROM ESTERS OF ARYLCHLOROBORIC ACIDS

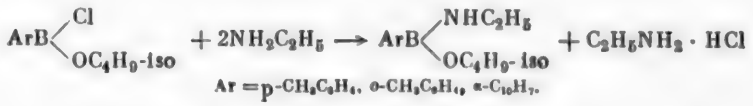
B. M. Mikhailov and T. V. Kostroma

Institute of Organic Chemistry, Academy of Sciences, USSR

It was previously shown [1] that at 270 – 300°, esters of phenylethylaminoboric and α-naphthylethylaminoboric acids, obtained by the action of ethylamine on appropriate esters of arylchloroboric acids, were converted into esters of arylboric acids and into B-triphenyl-N-triethylborazole and B-tri-α-naphthyl-N-triethylborazole, respectively.

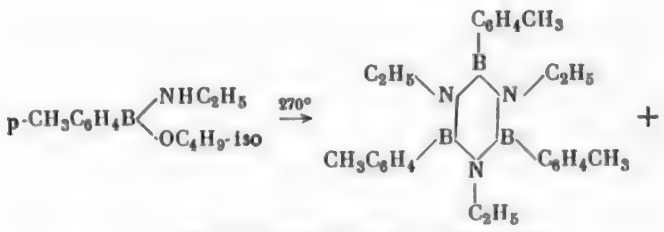
In order to extend this method of synthesizing borazole derivatives, we investigated the thermal conversions of some other esters of arylethylaminoboric acids and also esters of arylphenylaminoboric acids.

The isobutyl esters of p-tolylethylaminoboric, o-tolylethylaminoboric and α-naphthylethylaminoboric acids were obtained by the action of ethylamine on esters of arylchloroboric acids. The third ester had not been isolated in a pure form previously and was subjected to thermal conversion in an undistilled form [1].



Ar = p-$CH_3C_6H_4$, o-$CH_3C_6H_4$, α-$C_{10}H_7$. (1)

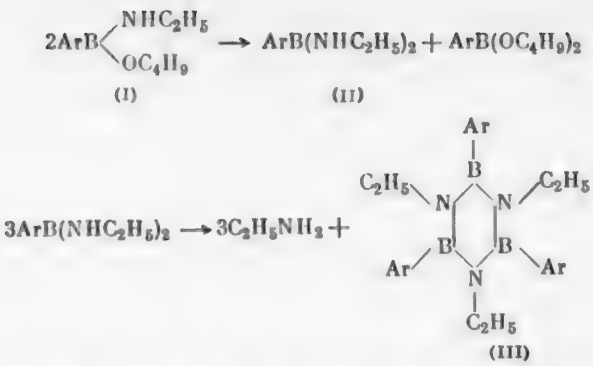
When heated for 1 hour at 260°, the isobutyl ester of p-tolylethylaminoboric acid was converted, like the esters investigated previously, into a mixture of B-tri-p-tolyl-N-triethylborazole and the isobutyl ester of p-tolylboric acid.



$+ p\text{-}CH_3C_6H_4B(OC_4H_9\text{-iso})_2 + NH_2C_2H_5$ (2)

In contrast to the other esters of arylethylaminoboric acids investigated, the isobutyl ester of o-tolylethylaminoboric acid was quite stable and did not form a borazole derivative when heated at 300° for several hours.

As regards the mechanism for the conversion of esters of arylethylaminoboric acids (I) into borazole compounds and esters of arylboric acids, we expressed the opinion [1] that it was simply symmetrization of the amino esters into a mixture of esters of arylboric acids and aryl-bis(ethylamino)-boron (II) and subsequent thermal conversion of the latter into a borazole derivative (III) by elimination of ethylamine.

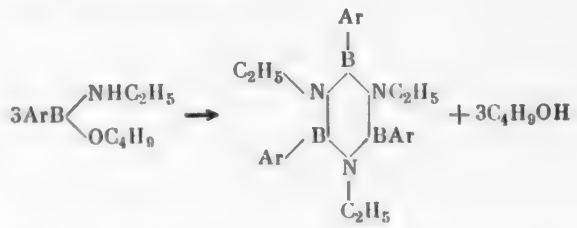


(3)

(4)

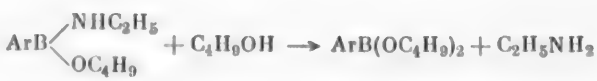
However, this mechanism does not agree with the fact that the thermal conversion of phenyl-bis(ethylamino)-boron into B-triphenyl-N-triethylborazole proceeds in low yield [2] (17%), while esters of arylethylaminoboric acids give borazole derivatives in good yields and, in particular, the yield of B-triphenyl-N-triethylborazole by this method was 72.6%, calculated according to equation (2).

Therefore, we proposed that the formation of borazole compounds proceeded directly from the amino esters (I) by elimination of alcohol from them (equation 5).



(5)

The alcohol then reacted with the original amino ester to form an ester of an arylboric acid and ethylamine according to equation (6).

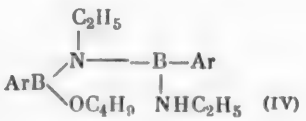


(6)

As a result, one half of the ester of the arylethylaminoboric acid was converted into a borazole compound and the second into an ester of an arylboric acid, as actually occurs.

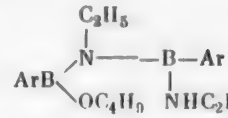
This reaction mechanism would be confirmed by the smooth conversion of aryl-bis(ethylamino)-boron (II) into B-triaryl-N-triethylborazole when heated in the presence of alcohol in a small amount in relation to (II). The alcohol would convert part of the diamine (II) into an ester of an arylethylaminoboric acid, which would then condense into a borazole compound and the regenerated alcohol would again react with the diamine (II).

Experiment showed that when phenyl-bis(ethylamino)-boron was heated at 260° in the presence of a very small amount of butyl alcohol, it was converted into B-triphenyl-N-triethylborazole in 85% yield, while in the absence of the alcohol, the yield of the borazole compound was only 17% [2], as has already been mentioned above. Thus, the mechanism presented above and represented by equations (5) and (6), is confirmed experimentally. The only thing remaining unclear is whether the alcohol is eliminated from one molecule of amino ester (I) and the borazole compound produced by trimerization of a "borazine", ArB = NR, or whether the elements of alcohol are eliminated from different molecules with the formation of an intermediate compound (IV), which then reacts with a third molecule of amino ester.

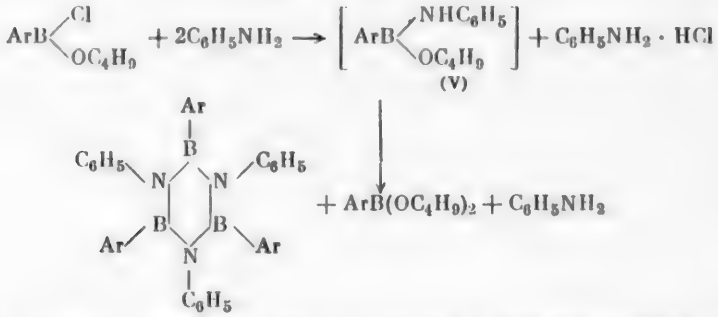


(IV)

With aniline, esters of arylchloroboric acids form aniline hydrochloride and esters of arylphenylaminoboric acids, which could not be obtained in an individual state. When distilled in vacuum at 15 – 20 mm, they decomposed to aniline, esters of arylboric acids and B-triaryl-N-triphenylborazoles. The reaction may be represented by the scheme below.



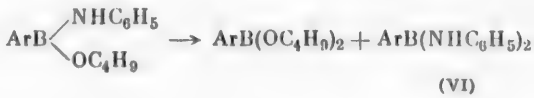
(IV)



(V)

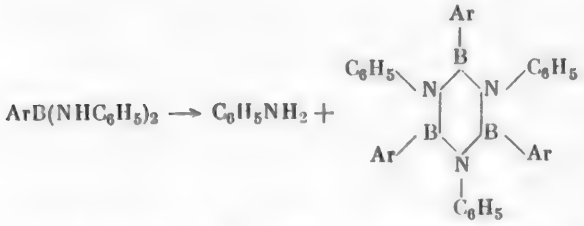
Thus, the ester of phenylchloroboric acid and aniline yielded hexaphenylborazole (in 30% yield) and the ester of p-tolylchloroboric acid and aniline gave B-tri-p-tolyl-N-triphenylborazole (39.4%).

The mechanism of the formation of borazole compounds from esters of arylphenylaminoboric acids is different from the mechanism of the thermal conversion of esters of arylethylaminoboric acids. In contrast to the latter, esters of arylphenylaminoboric acids symmetrize into esters of arylboric acids and aryl-bis(phenylamino)--boron (VI) at a temperature of about 200° (equation 7) and the latter are then converted into hexaarylborazoles with the elimination of aniline at 300 – 400° (equation 8).



(7)

(VI)



(8)

This mechanism is proved by the fact that we were able to isolate the aryl-bis(phenylamino)-borons formed in the first stage of the reaction (equation 7) in an individual state by thermal conversion of the amino esters in high vacuum; under these conditions, the aryl-bis(phenylamino)-borons formed distilled without decomposition.

In this way, from the ester of phenylphenylaminoboric acid we obtained a 79.4% yield, calculated on equation (7), of phenyl-bis(phenylamino)-boron and from the ester of p-tolylphenylaminoboric acid, p-tolyl-bis(phenylamino)-boron (83.6%).

In accordance with the mechanism given, borazole compounds were obtained from the amino esters (V) in the same yield (about 30%) as in the thermal decomposition of aryl-bis(phenylamino)-boron. Actually, heating phenyl-bis(phenylamino)-boron gave a 34% yield of hexaphenylborazole [2] and when p-tolyl-bis(phenylamino)--boron was heated at 400°, B-tri-p-tolyl-N-triphenylborazole was formed in 33.8% yield.

We should note that in the presence of a small amount of butyl alcohol, phenyl-bis(phenylamino)-boron was converted into hexaphenylborazole in the same yield as without alcohol.

All the aromatic derivatives of borazole obtained had unusual stability to atmospheric oxygen and moisture for organoboron compounds.

EXPERIMENTAL

Isobutyl ester of o-tolylethylaminoboric acid. 8.75 ml of ethylamine, diluted with 10 ml of ether, was added with stirring to 14.3 g of the isobutyl ester of o-tolylchloroboric acid in 20 ml of ether at -30° in a three-necked flask. After the addition, the reaction mixture was stirred at -30° for half an hour and for half an hour at room temperature. The precipitate of ethylamine hydrochloride liberated was removed by filtration and washed with ether. We obtained 6.09 g of $C_2H_5NH_2 \cdot HCl$ with m.p. 108 – 110°. After removal of the solvent from the filtrate, the residue was rapidly distilled from a Claisen flask at 96 – 100° (3.5 mm). A second distillation yielded 11 g of the isobutyl ester of o-tolylethylaminoboric acid with b.p. 93 – 95° (3 mm). The yield was 84%; n_D^{20} 1.4847, d_4^{20} 0.9042.

Found %: C 71.14; H 10.00; B 4.96. $C_{13}H_{22}ONB$. Calculated %: C 71.24; H 10.11; B 4.93.

The amino ester was a colorless liquid, which was very sensitive to moisture and atmospheric oxygen. When heated at 260° for 4 hours, it was not converted into a borazole, in contrast to the other amino esters.

Isobutyl ester of p-tolylethylaminoboric acid. With cooling to -30° and stirring, 9.68 g of ethylamine in 10 ml of ether was added to 22 g of the isobutyl ester of p-tolylchloroboric acid. The experiment was similar to the previous one. We obtained 10.1 g of ethylamine hydrochloride with m.p. 105 – 110°. The solvent was removed from the filtrate and the residue vacuum distilled. We obtained 16.2 g of the isobutyl ester of p-tolylethylaminoboric acid with b.p. 110 – 112° (2 mm). The yield was 59.4%; n_D^{20} 1.4891, d_4^{20} 0.9059.

Found %: C 71.50; H 10.09; B 4.90. $C_{13}H_{22}ONB$. Calculated %: C 71.70; H 10.11; B 4.93.

Isobutyl ester of α-naphthylethylaminoboric acid. With cooling to -30°, 10.9 g of ethylamine, diluted with 12 ml of ether, was added to 30 g of the isobutyl ester of α-naphthylchloroboric acid in 40 ml of ether. The reaction mixture was stirred for 1 hour and then the ethylamine hydrochloride collected (11.45 g; m.p. 107 – 110°). The solvent was removed and the residue vacuum distilled. We obtained 16.2 g of the isobutyl ester of α-naphthylethylaminoboric acid with b.p. 182 – 185 at 9 mm (yield 52.4%); n_D^{20} 1.5470, d_4^{20} 0.9750.

Found %: C 75.30; H 8.35; B 4.81. $C_{16}H_{22}ONB$. Calculated %: C 75.30; H 8.69; B 4.24.

We also obtained 5.1 g of the isobutyl ester of α-naphthylboric acid with b.p. 182 – 185° (9 mm).

B-Tri-p-tolyl-N-triethylborazole. 9.8 g of the isobutyl ester of p-tolylethylaminoboric acid was heated at 260° for 1 hour. The cooled reaction mixture was treated with isopentane and the precipitate collected and washed with isopentane. We obtained 1.2 g of B-tri-p-tolyl-N-triethylborazole with m.p. 222 - 225°. The solvent was removed and the residue fractionated. We obtained a mixture (5.64 g) of the isobutyl esters of p-tolylethylaminoboric acid and p-tolylboric acid, boiling at 155 – 165° (19 mm). The residue from the distillation was washed with isopentane. We obtained a further 0.7 g of borazole with m.p. 217 – 221°. The yield of borazole was 58.3%. After recrystallization from a mixture of benzene and isopentane, the product had m.p. 222 – 225° (in a sealed capillary).

Found %: C 74.28; H 8.65; B 7.69. M 415.27. $C_{21}H_{21}N_3B_3$. Calculated %: C 74.53; H 8.33; B 7.46. M 435.03.

Hexaphenylborazole. At room temperature, 18.62 g of aniline, diluted with 20 ml of ether, was added to 19.65 g of the isobutyl ester of phenylchloroboric acid in 20 ml of ether. After the addition, the reaction mixture was stirred for 1 hour further; the precipitate of aniline hydrochloride was collected (12.7 g; m.p. 196 – 198°) and washed with hot benzene. The solvent was removed in vacuum and the liquid residue fractionated. We obtained 3.7 g aniline with b.p. 88 – 91° (21 mm), which was identified as $C_6H_5NH_2 \cdot HCl$ (m.p. 198°) and 7.5 g of the isobutyl ester of phenylboric acid with b.p. 146 – 150° (21 mm).

Found %: Ar 32.50; B 4.31. $C_{14}H_{23}O_2B$. Calculated %: Ar 32.93; B 4.62.

The residue from the distillation was treated with hot xylene. We obtained 2.7 g of hexaphenylborazole (30% yield), which decomposed at 380 – 385° (in a sealed capillary) after 3 recrystallizations from benzene with isopentane.

Found %: C 80.56; H 5.95; B 5.95. $C_{36}H_{30}N_3B_3$. Calculated %: C 80.35; H 5.61; B 6.03.

B-Tri-p-tolyl-N-triphenylborazole. The experiment was similar to the one above. 16.1 g of the isobutyl ester of p-tolylchloroboric acid, 14.3 g of aniline and 40 ml of ether were used in the reaction. We obtained 12.1 g of aniline hydrochloride with m.p. 195 – 198°. After removal of the solvent, the residue was vacuum distilled. We obtained 3.8 g of aniline with b.p. 80 – 100° (15 mm) and 6.63 g of the isobutyl ester of p-tolylboric acid with b.p. 145 – 150° (10 mm).

Found %: Ar 37.1; B 4.21. $C_{15}H_{25}O_2B$. Calculated %: Ar 36.7; B 4.35.

The residue from the distillation was washed with isopentane. We obtained 2.8 g of B-tri-p-tolyl-N-triphenylborazole (39.4%), which had m.p. 282 – 284° (with decomp.) after 3 recrystallizations from a mixture of benzene and isopentane.

Found %: C 80.30; H 6.50; B 5.60. $C_{39}H_{36}N_3B_3$. Calculated %: C 80.87; H 6.26; B 5.60.

B-Triphenyl-N-triethylborazole. 2.1 g of phenyl-bis(ethylamino)-boron was heated at 270° with 0.2 ml of anhydrous isobutyl alcohol for 2 hours. The liberation of ethylamine was observed. The reaction mixture was cooled and the precipitate collected and washed with isopentane. We obtained 1.33 g of B-triphenyl-N-triethylborazole with m.p. 205 – 209° (a mixed melting point with B-triphenyl-N-triethylborazole was not depressed). The yield was 85.2%.

Phenyl-bis(phenylamino)-boron. At room temperature, 18.62 g of aniline, diluted with 20 ml of ether, was added to 19.6 g of the isobutyl ester of phenylchloroboric acid in 20 ml of absolute ether. After the addition of the aniline, the reaction mixture was stirred for an hour, then the crystals of aniline hydrochloride liberated (12.78 g; m.p. 195 – 198°) were collected and washed with hot benzene. The solvent was removed and the residue distilled in high vacuum. We isolated fractions: 1st 90 – 150° (0.06 mm), 10.2 g; 2nd 150 – 177° (0.06 mm), 1.1 g; 3rd 178 – 180° (0.06 mm), 11.1 g. A second distillation of the first fraction yielded 9 g of the isobutyl ester of phenylboric acid with b.p. 124 – 127° (9 mm), n_D^{20} 1.4750. The yield was 76.9%. The third fraction, which appeared as a thick oil, was phenyl-bis(phenylamino)-boron. After treatment with isopentane, the substance crystallized; m.p. 84 – 86°. The yield was 79.4%.

p-Tolyl-bis(phenylamino)-boron. The experiment was similar to the one above. 15.4 g of the isobutyl ester of p-tolylchloroboric acid in 20 ml of ether and 13.6 g of aniline, dissolved in 20 ml of ether, were used in the reaction. We obtained 10 g of aniline hydrochloride. Fractional distillation of the filtrate yielded the following fractions: 1st 81 – 85° (0.04 mm), 7.8 g; 2nd 86 – 162° (0.04 mm), 0.9 g; 3rd 163 – 165° (0.04 mm), 8.7 g. The first fraction was the isobutyl ester of p-tolylboric acid. The yield was 85.9%. The third fraction was p-tolyl-bis(phenylamino)-boron, which appeared as a thick, colorless oil and which crystallized on addition of isopentane. The substance had m.p. 100 – 102°. The yield was 83.6%.

Found %: C 79.92; H 6.76; B 3.70; N 10.10. $C_{19}H_{19}N_2B$. Calculated %: C 79.73; H 6.69; B 3.78; N 9.79.

Thermal conversion of p-tolyl-bis(phenylamino)-boron. 1.8 g of p-tolyl-bis(phenylamino)-boron in a two-necked flask with a distillation condenser, was heated on a metal bath. When the bath temperature reached 400°, aniline began to distill over. Over a period of 30 minutes, 0.56 g of aniline distilled. The residue was recrystallized from a mixture of benzene and pentane. We obtained 0.4 g (33.8%) of B-tri-p-tolyl-N-triphenylborazole; m.p. 282 – 284°.

SUMMARY

1. When heated to 270 – 300°, the esters of arylethylaminoboric acids were converted into a mixture of B-triaryl-N-triethylborazoles and esters of arylboric acids.

2. The action of aniline on esters of arylchloroboric acids formed esters of arylphenylaminoboric acids, which symmetrized into esters of arylboric acids and aryl-bis(phenylamino)-boron, when heated to 200°. When heated to 300 – 400°, the latter compounds were converted into a mixture of B-triaryl-N-triphenylborazoles and esters of arylboric acids.

3. A study was made of the mechanism of the thermal conversion of N-substituted esters of arylaminoboric acids.

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ORGANOBORON COMPOUNDS

XXXVII. SYNTHESIS OF B-TRIARYLBORAZOLES FROM ARYLBORON DICHLORIDES

B. M. Mikhailov, A. N. Blokhina and T. V. Kostroma

Institute of Organic Chemistry, Academy of Sciences, USSR

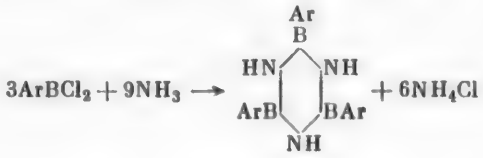
Previously [1] a description was given of the reaction between phenylboron dichloride and ammonia, which led to the formation of B-triphenylborazole. As the data from this investigation showed, other arylboron dichlorides reacted with ammonia in the same way.

The arylboron dichlorides required for the investigation were prepared by the reaction between esters of arylboric acids and phosphorus pentachloride [2]. In this way, good yields of p-tolylboron dichloride, p-chlorophenylboron dichloride and p-bromophenylboron dichloride were obtained.

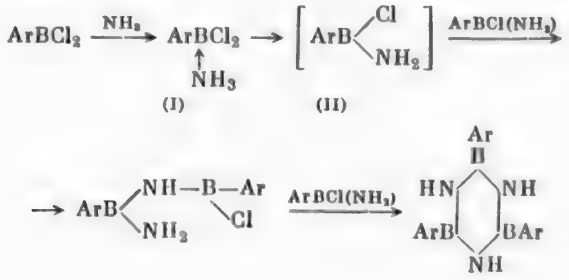
$$ArB(OR)_2 + 2PCl_5 \longrightarrow ArBCl_2 + 2POCl_3 + 2RCl.$$

When ammonia was passed into a benzene solution of an arylboron dichloride at room temperature, the ammoniate was formed. If the benzene suspension of the ammoniate was heated on a water bath and the input of ammonia continued, then under these conditions the ammoniate was converted into ammonium chloride and B-triarylborazole.

The method gave 65 – 91% yields of B-tri-p-tolylborazole, B-tri-p-chlorophenylborazole and B-tri-p-bromophenylborazole. The reaction may be represented by the following equation



The reaction mechanism probably consists of conversion of the initially formed ammoniate of the arylboron dichloride (I) into an arylaminoboron chloride (II), whose molecules then condense with each other to form a triarylborazole.



The stability of the B-triarylborazoles towards moisture and atmospheric oxygen was unusual for organoboron compounds. Phenylboron dichloride formed complexes with triethylamine.

EXPERIMENTAL

All operations with organic compounds of boron were performed in an atmosphere of nitrogen.

Phenylboron dichloride. The procedure for preparing phenylboron dichloride described previously [2] was changed somewhat. The reaction between the butyl ester of phenylboric acid (70 g) and phosphorus pentachloride (124 g) was carried out in a three-necked flask, fitted with a stirrer and a distillation condenser. The first half of the phosphorus pentachloride was added in portions with stirring and water cooling from a round-bottomed flask, connected to the third opening of the three-necked flask with rubber tubing, at such a rate that the temperature of the reaction mixture was about 70 – 80°. At the end of the reaction, the whole of the second half of the phosphorus pentachloride was added in one portion and the mixture was stirred and heated on a water bath for 1 hour. The stirrer was then replaced by a bung and the isobutyl chloride and phosphorus oxychloride were distilled from the reaction mixture under reduced pressure (80 – 100 mm). The residue was fractionated with a fractionating column and the fraction with b.p. 83 – 90° (33 mm) was again fractionated. The yield of phenylboron dichloride with b.p. 87 – 89° (37 mm) was 60%.

p-Tolylboron dichloride. With stirring and water cooling, half of the phosphorus pentachloride (53.2 g) was gradually added to 63.4 g of the isobutyl ester of p-tolylboric acid in a three-necked flask. At the end of the reaction, the isobutyl chloride and phosphorus oxychloride were removed under reduced pressure and then the second half of the phosphorus pentachloride (53.2 g) added in one portion; with stirring, the reaction mixture was carefully heated with a burner so that the alkyl halide formed distilled at atmospheric pressure. When the vapor temperature reached 82 – 84°, the phosphorus halide disappeared and the reaction mixture began to darken. The reaction mixture was cooled, transferred to a Favorskii flask and fractionated. We obtained 22.1 g of p-tolylboron dichloride with b.p. 91 – 94° (7 mm) and m.p. 25 – 27°. The yield was 50%.

Found %: C 48.48; H 4.22; B 6.06; Cl 40.56. $C_7H_7Cl_2B$. Calculated %: C 48.71; H 4.13; B 6.24; Cl 41.04.

According to data in [3], the m.p. is 27°; the authors did not give the boiling point or the yield.

p-Bromophenylboron dichloride. 61.3 g of the isobutyl ester of p-bromophenylboric acid and 81.2 g of phosphorus pentachloride were used in the experiment. The experiment was similar to the one above. Fractional distillation of the reaction products yielded 30 g of crystalline p-bromophenylboron dichloride with b.p. 110 – 116° (11 mm), which represents 66.3%. After additional distillation, the substance had b.p. 114 – 114.5° (20 mm) and m.p. 36 – 38°.

Found %: C 30.54; H 1.70; halogen 62.78; B 4.35. $C_6H_4Cl_2BrB$. Calculated %: C 30.31; H 1.70; halogen 63.52; B 4.53.

B-Tri-p-tolylborazole. 4.3 g of p-tolylborondichloride was dissolved in 50 ml of benzene and a stream of dry ammonia passed into the solution for 30 minutes, when heat was evolved and a colorless precipitate formed. The passage of ammonia was then continued for 1 hour, while the reaction mixture was heated on a water bath. After being centrifuged, the solution was decanted from the ammonium chloride (2.85 g) and evaporated to dryness. To the residue (2.4 g) was added isopentane and the precipitate collected and washed with isopentane. We obtained 1.8 g of B-tri-p-tolylborazole with m.p. 179 – 182° (64.3%). After recrystallization from a mixture of benzene and isopentane, the substance had m.p. 189 – 190° (in a sealed capillary) and did not depress the melting point of a sample of B-tri-p-tolylborazole obtained previously [1].

B-Tri-p-bromophenylborazole. The experiment was similar to the previous one. 6.3 g of p-bromophenylboron dichloride in 50 ml of benzene was used in the reaction. At the end of the reaction, the mixture was cooled and the precipitate which formed was collected and treated with 200 ml of boiling benzene. The insoluble ammonium chloride (3 g) was filtered off and the benzene solution concentrated to small volume. 2.1 g of B-tri-p--bromophenylborazole crystallized in the form of colorless needles with m.p. 291 – 293° (in a sealed capillary). Concentration of the mother solution yielded a further 0.8 g of the borazole derivative with m.p. 290 – 293°. The main benzene solution yielded a further 0.3 g of substance with m.p. 292 – 293°. The total yield of B-tri--p-bromophenylborazole was 3.2 g (66.5%).

Found %: C 39.60; H 2.67; B 6.29; Br 43.24; N 7.68. $C_{18}H_{15}Br_3N_3B_3$. Calculated %: C 39.63; H 2.77; B 5.95; Br 43.94; N 7.69.

The substance was soluble in ether and benzene and insoluble in pentane and hexane.

B-Tri-p-chlorophenylborazole. The experiment was similar to the preparation of B-triphenylborazole. 4.8 g of p-chlorophenylboron dichloride in 40 ml of benzene was used in the reaction. We obtained 2.8 g of ammonium chloride and 3.1 g of B-tri-p-chlorophenylborazole with m.p. 263 – 265°. The yield was 91.3%. After recrystallization from a mixture of benzene and isopentane, the substance had m.p. 269 – 270° (in a sealed capillary).

Found %: C 52.31; H 3.69; B 7.45; Cl 25.73. M 416.11. $C_{18}H_{15}N_3Cl_3B_3$. Calculated %: C 52.43; H 3.66; B 7.87; Cl 25.83. M 412.28.

The substance was soluble in ether and benzene and insoluble in pentane and hexane.

Phenyltriethylaminoboron dichloride. 2.7 g of phenylboron dichloride was dissolved in 3 ml of ethyl ether with cooling to -10° and the solution added to an ether solution of triethylamine, cooled to -70°. A white precipitate formed immediately. The precipitate was collected and washed with ether. We obtained 3 g of a substance with m.p. 80 – 84° (in a sealed capillary).

Found %: B 3.92; Cl 27.15. $C_{12}H_{20}Cl_2NB$. Calculated %: B 4.16; Cl 27.30.

SUMMARY

By the action of ammonia at 80°, arylboron dichlorides were converted into B-triarylborazoles.

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THE REACTION OF PHOSGENE WITH TRIALKYL PHOSPHITES

K. A. Petrov, N. K. Bliznyuk and V. E. Burygin

In the synthesis of organophosphorus compounds with a phosphorus-carbon bond, use is very frequently made of dialkyl and trialkyl phosphites and by alkylation of these, a large number of different alkylphosphonates have been prepared. Thus, reaction of trialkyl phosphites with alkyl halides (the A. E. Arbuzov reaction) gives good yields of dialkylphosphonates. Reaction of sodium salts of dialkyl phosphites with alkyl halides (the Michaelis--Becker reaction) also yields esters of alkylphosphinic acids. These two interesting reactions have been used by many investigators for the synthesis of various organophosphorus compounds.

M. I. Kabachnik and P. A. Rossiiskaya showed that acyl halides react smoothly with trialkyl phosphites by a type of "Arbuzov rearrangement" with the formation of esters of α-ketophosphinic acids, $RCOPO(OR')_2$ [1], which showed clearly expressed carbonyl reactions [2]. These authors then attempted to extend the reaction of acyl halides with phosphites to other examples and studied the interaction of trimethyl phosphite with phosgene [3]. On the basis of data obtained, they considered that like acyl chlorides, phosgene reacted with trimethyl phosphite by a type of A. E. Arbuzov reaction with the liberation of methyl chloride and the formation of an ester of chloroformylphosphinic acid, $ClCOP(O)(OCH_3)_2$. By the action of a second molecule of phosphite on the ester of chloroformylphosphinic acid, they naturally considered that the ester of carbonyldiphosphinic acid, $(CH_3O)_2P(O)-CO-P(O)(OCH_3)_2$ was formed.

Ford-Moore [10] had previously shown that triisopropyl and triethyl phosphites reacted with phosgene, with the formation of chlorophosphates and not esters of chloroformylphosphinic acid. We studied the reaction considered and definitely proved the structure of the reaction products. The action of phosgene on trimethyl phosphite under the conditions described by M. I. Kabachnik and P. A. Rossiiskaya gave a good yield of dimethyl chlorophosphate and not the ester of chloroformylphosphinic acid. The reaction of the phosphite with phosgene proceeded with the evolution of not only methyl chloride, as was shown by M. I. Kabachnik and P. A. Rossiiskaya, but also carbon monoxide, which we also isolated in quantitative yield and identified. The evolution of carbon monoxide occurred immediately after the beginning of the passage of phosgene into the phosphite. Apparently, with trimethyl phosphite, phosgene formed the ester of chloroformylphosphinic acid and due to its instability, the latter immediately decomposed even at low temperatures with the formation of carbon monoxide and dimethyl chlorophosphate.

$$COCl_2 + P(OCH_3)_3 \longrightarrow [ClCOP(O)(OCH_3)_2] + CH_3Cl$$
$$\downarrow$$
$$CO + (CH_3O)_2POCl$$

Dimethyl chlorophosphate was obtained in 78% yield as a colorless liquid with b.p. 70° (12 mm), d_4^{20} 1.3320 and n_D^{20} 1.4123. Dimethyl chlorophosphate, which we obtained by the reaction of dimethyl phosphite with sulfuryl chloride, had b.p. 67 – 69° (11 mm), d_4^{20} 1.3317, n_D^{20} 1.4120. According to data given in [4], the b.p. is 60° (4 mm). Dimethyl chlorophosphate, obtained by the reaction of trimethyl phosphite with phosgene, reacted with aniline to give the anilide of dimethylphosphoric acid, which melted at 88.5° after recrystallization from water (refer to data [5]: m.p. 88 – 88.5°). For identification of this anilide, an anilide was prepared from the chlorophosphate, obtained by treatment of dimethyl phosphite with sulfuryl chloride. The anilide had m.p. 88.5°. A mixed melting point of the two anilides was not depressed.

Thus, it can be accepted that the action of phosgene on trimethyl phosphite yields dimethyl chlorophosphate and that the data of M. I. Kabachnik and P. A. Rossiiskaya on this subject are incorrect. Meanwhile, there are certain peculiarities in the analysis results presented by these authors: the difference in the phosphorus contents of dimethyl chlorophosphate and the dimethyl ester of chloroformylphosphinic acid is more than 3%, i.e. far beyond the limits of the accuracy of the analysis.

We also showed that, like trimethyl phosphite, triethyl phosphite reacts readily with phosgene with the formation of a chlorophosphate and not an ester of chloroformylphosphinic acid. As in the case of trimethyl phosphite, the reaction proceeded with the evolution of carbon monoxide and alkyl halide, which were obtained in practically quantitative yields. The diethyl chlorophosphate was converted into the anilide (m.p. 94–95°) and compared with the anilide obtained from the chlorophosphate, synthesized by the reaction of diethyl phosphite with sulfuryl chloride or chlorine (m.p. 94–95°). According to data given in [6], the anilide of diethyl phosphoric acid melts at 94–95°. A mixed melting point of the two anilides was not depressed.

The reaction of phosgene with phosphites forms chlorophosphates; therefore, it can be accepted that the data of M. I. Kabachnik and P. A. Rossiiskaya on the preparation of an ester of carbonyldiphosphinic acid is also incorrect. Since an ester of chloroformylphosphinic acid was not obtained, an ester of carbonyldiphosphinic acid could not have been obtaind. Without having the latter, these authors could not have obtained a nitrophenylhydrazone or a semicarbazone and, without doubt, did not have the hydrate of the ester of carbonyldiphosphinic acid. In this case also, it is surprising that the substances obtained gave good phosphorus analysis results.

In the present work it was shown that chlorophosphates react with trialkyl phosphites by a type of Arbuzov reaction with the evolution of alkyl chloride and the formation of an ester of diphosphonic acid with a P-P bond. *

$$(RO)_2P(O)Cl + (RO)_3P \longrightarrow (RO)_2P(O)-P(O)(OR)_2 + RCl$$

It is quite possible that M. I. Kabachnik and P. A. Rossiiskaya mistakenly accepted the tetramethyl ester of diphosphonic acid with a P-P bond as an ester of carbonyldiphosphinic acid.

Diphosphonates with a P-P bond are unstable substances. On distillation, they are often decomposed with the formation of esters of alkylphosphinic acids and metaphosphates.

$$(RO)_2P(O)-P(O)(OR)_2 \longrightarrow R-P(O)(OR)_2 + ROPO_2$$

This decomposition proceeds during the preparation process and during distillation, even in high vacuum. The alkylphosphinic ester, isolated in an individual state, was hydrolyzed to the alkylphosphinic acid, which was converted into the aniline salt. The aniline salt was identified by comparison of melting point and by a mixed melting point with the aniline salt of the alkylphosphinic acid, obtained from the alkyl phosphonate, which was synthesized by A. E. Arbuzov's method.

The diphosphonate was decomposed by water; the reaction products reduced mercuric to mercurous chloride. Evidently, the hydrolysis had proceeded with rupture of the P-P bond and formation of phosphite and phosphate.

$$(RO)_2P(O)-P(O)(OR)_2 + H_2O \longrightarrow (RO)_2POH + (RO)_2P(O)-OH$$

We have to assume that the mixture of dialkyl phosphite and dialkyl phosphate, formed by hydrolysis of the diphosphonate with an equivalent amount of water was taken by M. I. Kabachnik and P. A. Rossiiskaya for the hydrate of the ester of carbonyldiphosphinic acid.

* The isomer of the diphosphonate with a P-P bond is a subphosphate and the formation of this in the given reaction is not excluded.

The ester of the diphosphinic acid with a P-P bond was readily cleaved with chlorine and sulfuryl chloride with the formation of a dialkyl chlorophosphate. The dialkyl chlorophosphates were isolated in a discrete state, analyzed and converted into anilides of dialkylphosphoric acids.

The reaction of chlorophosphates with neutral phosphites was studied by reacting dimethyl and diethyl chlorophosphates with trimethyl and triethyl phosphites, respectively.

EXPERIMENTAL

Reaction of trimethyl phosphite with phosgene. 14.85 g of dry phosgene was slowly (over a period of 3 hours) passed into 18.6 g of trimethyl phosphite with water cooling. The outlet from the reaction flask with the phosphite was successively connected to a trap cooled to -78°, a bottle with alkali and then a gasometer. Several minutes after the input of phosgene was begun, a gas started to collect in the gasometer and a liquid condensed in the trap. Methyl chloride, 7.4 g, (97%), was obtained from the trap. In the gasometer we collected 3.3 liters (98%) of a gas, which burned with a bluish flame, reduced an ammonia solution of silver nitrate and did not contain halogen. The gas was carbon monoxide. Distillation of the reaction product in vacuum yielded 16.9 g (78%) of a colorless, transparent liquid [b.p. 70° (12 mm), d_4^{20} 1.3320, n_D^{20} 1.4123], which was found to be dimethyl chlorophosphate.

Found %: Cl 24.7. $C_2H_6O_3PCl$. Claculated %: Cl 24.6.

Dimethyl chlorophosphate, obtained by the action of sulfuryl chloride on dimethyl phosphite, had the following constants:

b.p. 67 – 69° (11 mm), d_4^{20} 1.3317, n_D^{20} 1.4120. Literature data: b.p. 60° (4 mm) [4].

Anilide of the dimethyl ester of phosphoric acid. A solution of 2.82 g of aniline in 15 ml of dry ether was added dropwise to an ice-water cooled solution of 2.17 g of dimethyl chlorophosphate (obtained by the reaction of trimethyl phosphite with phosgene) in 15 ml of the same solvent. When the reagents were mixed, a precipitate of aniline hydrochloride formed immediately. The reaction mixture was left overnight and then the aniline hydrochloride removed by filtration; the solvent was removed from the filtrate and the residue recrystallized. We obtained 2.4 g (79.5%) of the anilide of dimethyl phosphate with m.p. 88.5° (from water). Literature data: m.p. 88 – 88.5° [5]. The anilide of dimethyl phosphate, obtained under analogous conditions from dimethyl chlorophosphate, synthesized by chlorination of dimethyl phosphite, had the same melting point. A mixed melting point of these two anilides was not depressed.

Reaction of trimethyl phosphite with dimethyl chlorophosphate. 12.4 g of trimethyl phosphite was added dropwise to 14.45 g of dimethyl chlorophosphate in a Claisen flask, fitted with a thermometer and a dropping funnel, and heated on a water bath. The outlet of the flask was connected to a trap cooled to -78°. The reaction began at 90° and was complete after 30 – 40 minutes. The end of the reaction was determined by the absence of chlorine from the reaction mixture. Methyl chloride (4 g; 80%) was condensed in the trap. Distillation of the reaction product yielded two fractions: 1st 38 – 40° (0.6 mm), 3.9 g; 2nd 114 – 116° (0.6 mm), 9 g; d_4^{20} 1.3360, n_D^{20} 1.4254. A second distillation of the 1st fraction yielded 3.5 g of a substance with b.p. 66 – 67° (12 mm), d_4^{20} 1.1735, n_D^{20} 1.4101, which was found to be the dimethyl ester of methylphosphinic acid. Literature data: b.p. 67° (12 mm), d_0^{20} 1.1741, n_D^{20} 1.4105 [7]. Hydrolysis of 2 g of the ester with hydrochloric acid yielded 1.2 g (80%) of methylphosphinic acid and by the usual method, this yielded 2.1 g (90%) of the aniline salt with m.p. 148 – 150° (from propyl alcohol). The aniline salt, synthesized from methylphosphinic acid, obtained from the diacid chloride, had the same melting point. A mixed melting point of these two salts was not depressed. The 2nd fraction was the tetramethyl ester of diphosphonic acid with a P-P bond.

Found %: P 28.2. $C_4H_{12}O_6P_2$. Calculated %: P 28.4.

A second distillation of the diphosphonate again formed two fractions: the first was the dimethyl ester of methylphosphinic acid (about 40%) and the second was the ester of diphosphonic acid (about 50%). An undistillable solid residue (methyl metaphosphate) remained in the flask.

Reaction of the tetramethyl ester of diphosphonic acid with sulfuryl chloride. With cooling in ice-water and stirring, a solution of 1.35 g of sulfuryl chloride in 10 ml of dry carbon tetrachloride was slowly added to 2.18 g of the tetramethyl ester of diphosphonic acid in 10 ml of the same solvent. Vacuum distillation yielded 0.5 g (17%) of dimethyl chlorophosphate with b.p. 66 – 67° (10 mm), d_4^{20} 1.3321, n_D^{20} 1.4123.

Found %: Cl 24.5. $C_2H_6O_3PCl$. Calculated %: Cl 24.6.

The anilide obtained from this chlorophosphate under the conditions described above had m.p. 88 – 89°.

Reaction of triethyl phosphite with phosgene. Under conditions similar to the reaction of trimethyl phosphite with phosgene, 16.6 g of triethyl phosphite and 9.9 g of phosgene yielded 6.1 g (94%) of ethyl chloride with b.p. 12 – 13° and 2 liters (90%) of carbon monoxide. Fractional distillation of the reaction product yielded 12 g (70%) of diethyl chlorophosphate with b.p. 79.5 – 80° (10 mm), d_4^{20} 1.2002, n_D^{20} 1.4192.

Found %: Cl 20.5. $C_4H_{10}O_3PCl$. Calculated %: Cl 20.6.

Diethyl chlorophosphate, obtained by the action of sulfuryl chloride or chlorine on diethyl phosphite, had b.p. 76 – 77° (8 mm), d_4^{20} 1.2005, n_D^{20} 1.4191. Literature data: b.p. 93 – 94° (10 mm) [8]. The anilide of diethyl phosphate, obtained from this chlorophosphate by the method described above, melted at 94 – 95° (yielded 70.5%). The anilide, obtained from the chlorophosphate synthesized by chlorination of diethyl phosphite, had the same melting point. Literature data: m.p. 94 – 95° [6]. A mixed melting point of the two anilides was not depressed.

Reaction of triethyl phosphite with diethyl chlorophosphate. 16.6 g of triethyl phosphite was slowly added to 17.25 g of diethyl chlorophosphate in a Claisen flask, fitted with a thermometer and a dropping funnel, heated to 145 – 155° on a paraffin bath. The outlet of the flask was connected to a cooled (acetone and carbon dioxide) trap. The end of the reaction was determined by the absence of chlorine from the reaction mixture. Ethyl chloride (5.4 g, 84%; b.p. 12 - 13°) condensed in the trap. Fractional distillation of the reaction product in vacuum yielded two fractions: 1st 43 – 45° (0.8 mm) 4.5 g; 2nd 130° (0.8 mm), 16 g; d_4^{20} 1.1492, n_D^{20} 1.4200. A second distillation of the first fraction yielded 3.9 g of a substance with b.p. 87 – 88° (9 mm), d_4^{20} 1.0260, n_D^{20} 1.4165, the diethyl ester of ethylphosphinic acid. Literature data: b.p. 86 – 88° (9 mm), d_4^{20} 1.0259, n_D^{20} 1.4163 [9]. Hydrolysis of 2.5 g of the ester with hydrochloric acid yielded 1.5 g (91%) of ethylphosphinic acid and by the normal method this yielded 2 g (72%) of an aniline salt with m.p. 143 – 145° (from propyl alcohol). The aniline salt, synthesized from ethylphosphinic acid, which was obtained by hydrolysis of the diethyl ester of ethylphosphinic acid, prepared by Arbuzov's method, had the same melting point. A mixed melting point of the two salts was not depressed. The second fraction was the tetraethyl ester of diphosphonic acid with a P-P bond.

Found %: P 22.5. $C_8H_{20}O_6P_2$. Calculated %: P 22.6.

A second distillation of the diphosphonate again yielded two fractions: the first was the diethyl ester of ethylphosphinic acid (~35%) and the second was the ester of diphosphonic acid (~55%). An undistillable solid residue (ethyl metaphosphate) remained in the flask.

Reaction of the tetraethyl ester of diphosphinic acid with sulfuryl chloride. Under conditions analogous to those described above, 2.74 g of the tetraethyl ester of diphosphonic acid and 1.35 g of sulfuryl chloride yielded 1.0 g (29%) of diethyl chlorophosphate with b.p. 78 – 80° (10 mm), d_4^{20} 1.2003, n_D^{20} 1.4192.

Found %: Cl 20.8. $C_4H_{10}O_3PCl$. Calculated %: Cl 20.6.

The anilide, obtained from this chlorophosphate under the conditions described above, melted at 94 – 95°.

SUMMARY

1. It was shown that phosgene reacts with neutral phosphites with the formation of dialkyl chlorophosphates, alkyl halides and carbon monoxide.

2. Dialkyl chlorophosphates react with neutral phosphites with the formation of tetraalkyl esters of diphosphinic acids with a P-P bond or subphosphates, isomeric with them.

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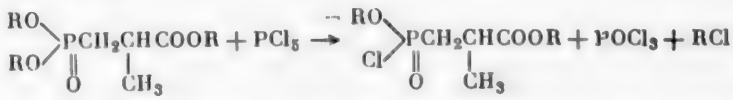
ANHYDRIDES OF PHOSPHONOISOBUTYRIC ACID. III

K. A. Petrov, A. A. Neimysheva and E. V. Smirnov

It is known that by the action of phosphorus pentachloride, phosphonocarboxylic acids and their esters are comparatively readily converted into acid chlorides of phosphonocarboxylic acids.* With this method, by changing the reaction conditions and the reagent ratios and also by using free acids in some cases and esters in others, it is possible to obtain mono-, di- and triacid chlorides of phosphonocarboxylic acids. At the present time the triacid chloride of phosphonoacetic and the P-mono- and P-diacid chlorides of esters of phosphonoacetic and phosphonopropionic acids are known. Mixed internal anhydrides, formed through the phosphoric acid and carboxylic acid residues, are completely unknown.

In the present work we describe the monoacid chlorides of esters of phosphonoisobutyric acid and internal cyclic anhydrides of phosphonocarboxylic acids.

The P-monoacid chlorides were synthesized by the interaction of phosphorus pentachloride with neutral esters of phosphonoisobutyric acid.



The acid chlorides were obtained in good yield if the reaction was performed in an inert solvent at 60 – 70° with a molar ratio of the reacting substances of 1 : 1. With an excess of phosphorus pentachloride and at a higher temperature, a mixture of substances was obtained consisting of P-mono- and P-diacid chlorides, from which the P-monoacid chloride could not be isolated in a discrete state by fractional distillation. By this method we obtained acid chlorides of the dimethyl, diethyl and ethyl butyl esters of phosphonoisobutyric acid. The position of the chlorine in the acid chlorides was not determined in this case since in other examples it was previously established that with the given temperature conditions and reagent ratios only P-monoacid chlorides of phosphonocarboxylic acids were obtained.

The acid chlorides of diesters of phosphonoisobutyric acid were colorless liquids, which distilled only at reduced pressure; they were hydrolyzed comparatively readily by water and their thermal stability increased with an increase in the number of carbon atoms in the ester group.

When trimethyl phosphonoisobutyrate was reacted with PCl_5 at a temperature above 70°, together with the acid chloride we also isolated a substance with b.p. 101 – 102° (0.1 mm), which did not contain chlorine and whose properties were different from those of the original ester. This substance was formed as a result of decomposition of the acid chloride on long standing and also on heating. From elementary analysis, structure (I) or (II) may be ascribed to the substance. These compounds may be formed as a result of intramolecular elimination of methyl chloride from the acid chloride of the dimethyl ester of phosphonoisobutyric acid.

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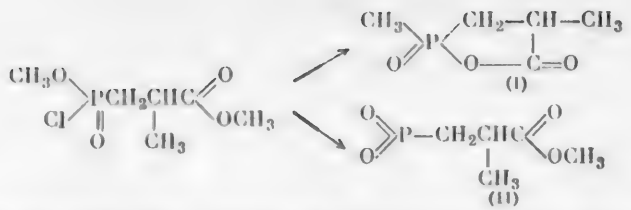
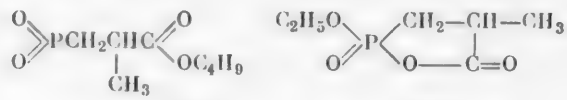


(I) (II)

The substance we obtained undoubtedly corresponded to structure (I), since compounds with structure (II) are metaphosphonates and must be undistillable solid substances.

The acid chloride of diethyl phosphonoisobutyrate also decomposed on prolonged heating at 150 – 170° and evolved ethyl chloride to form an internal anhydride of the P-ethyl ester of phosphonoisobutyric acid. The fact that the substance obtained was an internal cyclic anhydride was confirmed by its formation from the acid chloride of the P-ethyl C-butyl ester of phosphonoisobutyric acid. Had the thermal decomposition eliminated ethyl chloride and not butyl chloride, the C-butyl ester of the metaphosphonocarbonate (III) would have been formed and this would have differed in constants and elementary composition from the internal cyclic anhydride (IV).



(III) (IV)

The phosphorus, carbon and hydrogen contents and the molecular refraction found corresponded to those calculated for the anhydride of the P-ethyl ester of phosphonoisobutyric acid.

The internal anhydrides of P-esters of phosphonoisobutyric acid were readily hydrolyzed by water with the formation of dibasic acids, which required exactly two equivalents of alkali for titration. The P-methyl ester of phosphonoisobutyric acid was isolated in the form of the silver salt. Alkylation of the salt with methyl iodide yielded the trimethyl ester of phosphonoisobutyric acid.

EXPERIMENTAL

P-Acid chloride of dimethyl phosphonoisobutyrate. a) Over a period of half and hour with continuous stirring and water cooling, 23.2 g of phosphorus pentachloride was added in small portions to a solution of 23.4 g of the trimethyl ester of phosphonoisobutyric acid in 25 ml of carbon tetrachloride. To complete the reaction, the mixture was heated on a water bath, whose temperature was raised to 70° over a period of 2 hours and kept at this temperature for another hour. The unreacted PCl_5 was decomposed with a stream of dry sulfur dioxide and then the solvent and volatile substances were removed under reduced pressure and the residue fractionated. A second distillation yielded 17.75 g (74.5%) of the acid chloride of dimethyl phosphonoisobutyrate.

B.p. 104 – 105° (1 mm), d_4^{23} 1.2675, n_D^{22} 1.4560, MR 46.00; Calc. 46.02.

Found %: P 14.38; Cl 16.32. $C_6H_{12}O_4PCl$. Calculated %: P 14.45; Cl 16.55.

The acid chloride could be stored for a long period in the pure form without decomposition.

b) When reacted on a boiling water bath for 3 hours and the reaction mixture subsequently distilled, 17.8 g of trimethyl phosphonoisobutyrate and 17.6 g of phosphorus pentachloride in 20 ml of carbon tetrachloride yielded two fractions: 1st 123 – 124° (6 mm), 5.5 g; 2nd 163 – 164° (6 mm), 4.7 g (with partial decomposition). The material of the first fraction had a high chlorine content (19.3%) in comparison with that calculated for the monoacid chloride. It was impossible to obtain the monoacid chloride of dimethyl phosphonoisobutyrate in a chemically pure form by many distillations. After a second distillation, the second fraction yielded a substance corresponding to the anhydride of methyl phosphonoisobutyrate.

B.p. 100 – 102° (0.1 mm), d_4^{22} 1.3004, n_D^{23} 1.4520, MR 34.02; Calc. 33.97.

Found %: C 36.80; H 5.53; P 18.76. $C_5H_9O_4P$. Calculated %: C 36.59; H 5.49; P 18.90.

The anhydride of methyl phosphonoisobutyrate was hydrolyzed by water with the formation of the corresponding acid, which could be titrated with alkali. Titration of a 0.1240 g sample required 13.6 ml of 0.1 N alkali, which corresponds to the theoretically calculated amount for a dibasic acid.

The anhydride obtained was hydrolyzed and converted into the silver salt of the P-methyl ester of phosphonoisobutyric acid, alkylation of which yielded the starting ester. To a solution of 4 g of the anhydride, neutralized to phenolphthalein with 0.1 N alkali, was added a saturated solution of 8.3 g of silver nitrate and a white precipitate of the silver salt formed immediately. The precipitate was collected, washed with a small amount of water and dried in air. We obtained 4.7 g of salt.

Found %: Ag 54.41. $C_5H_9O_5PAg_2$. Calculated %: Ag 54.52.

Alkylation of the silver salt by heating with methyl iodide in chloroform solution yielded the trimethyl ester of phosphonoisobutyric acid.

Found %: P 14.36. $C_7H_{15}O_5P$. Calculated %: P 14.76.

P-Acid chloride of diethyl phosphonoisobutyrate. Under the conditions described for the preparation of the acid chloride of methyl phosphonoisobutyrate (Exp. "a"), 21.5 g of triethyl phosphonoisobutyrate and 17.6 g of phosphorus pentachloride in 20 ml of carbon tetrachloride yielded 16 g of the acid chloride of diethyl phosphonoisobutyrate. The yield was 78.5%.

B.p. 115 – 116° (1 mm), d_4^{22} 1.1695, n_D^{22} 1.4489, MR 55.61; Calc. 55.26.

Found %: Cl 14.65. $C_8H_{16}O_4PCl$. Calculated %: Cl 14.64.

Prolonged heating of the acid chloride at 150 – 170° produced thermal decomposition with the liberation of ethyl chloride and the formation of the anhydride of the P-ethyl ester of phosphonoisobutyric acid. The colorless liquid was readily hydrolyzed by water with the formation of the P-ethyl ester of phosphonoisobutyric acid.

Titration of 0.0818 g required 8.98 ml of 0.1 N KOH; according to calculation, a dibasic acid should require 9.19 ml; b.p. 154° (4 mm), d_4^{21} 1.2249, n_D^{21} 1.4550, MR 39.43; Calc. 38.58.

Found %: P 16.88. $C_6H_{11}O_4P$. Calculated %: P 17.42.

Acid chloride of P-ethyl C-butyl ester of phosphonoisobutyric acid. The acid chloride was obtained from the diethyl C-butyl ester of phosphonoisobutyric acid and PCl_5 under the conditions presented above.

B.p. 130 – 132° (2 mm), d_4^{19} 1.1617, n_D^{20} 1.4452.

Found %: Cl 13.59, $C_{10}H_{20}O_4PCl$. Calculated %: Cl 13.12.

When the acid chloride of the P-ethyl C-butyl ester of phosphonoisobutyric acid was heated to 180 – 190° for 6 hours, decomposition occurred with the liberation of butyl chloride and the formation of the anhydride of the P-ethyl ester of phosphonoisobutyric acid.

B.p. 129 — 130° (2.5 mm), d_4^{20} 1.2304, n_D^{19} 1.4523, MR 39.05; Calc. 38.58.

Found %: C 40.89; H 6.46; P 16.92. $C_6H_{11}O_4P$. Calculated %: C 40.45; H 6.18; P 17.42.

SUMMARY

Three P-acid chlorides of esters of phosphonoisobutyric acid were obtained. It was shown that during prolonged storage and also on heating, they decomposed with the formation of internal anhydrides of esters of phosphonoisobutyric acid.

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REACTIONS OF ALIPHATIC AMINES WITH β-CHLOROETHANESULFONYL CHLORIDES

K. A. Petrov and A. A. Neimysheva

The reactions of aromatic amines with β-chloroethanesulfonyl chloride were first investigated by Leymann [1], who isolated β-phenylaminoethanesulphonanilide and ethylenesulfonanilide by the action of aniline on the sulfonyl chloride in ether solution. The structure of the etheylenesulfonanilide was established by other investigators [2]. This reaction was studied in detail by Goldberg [3] and Kostosova [4]. Cyclohexylamine was reacted with the sulfonyl chloride and this gave cyclohexylaminoethanesulfoncyedohexylamide [3]. Up to now, no dialkylamindes of vinylsulfonic acid have been described in the literature. Attempts to prepare them by the action of aliphatic amines on β-chloroethanesulfonyl chloride did not give a positive result.

In this work, conditions were found under which the action of dimethylamine and diethylamine on β-chloroethanesulfonyl chloride yielded vinylsulfondialkylamides and dialkylaminoethanesulfondialkylamides. The reaction was carried out in ether or chloroform at various temperatures (from -10 to +60°) and with molar ratios of the sulfonyl chloride to amine of 1 : 3. In all cases the same products were obtained. In the isolation of the vinylsulfondialkylamides, the reaction mixture was washed with water, acidified with HCl, which removed the excess amine and the dialkylaminoethanesulfondialkylamides. The solvent was removed from the organic layer and the residue distilled to give the vinylsulfondialkylamides. The substances formed by the action of amines on β-chloroethanesulfonyl chloride could also be isolated conveniently by the following method: the amine hydrochloride was first separated by filtration and then dry hydrogen chloride was passed through the ether solution and the precipitated salt of the dialkylaminoethanesulfondialkylamide was collected. The free base was isolated by treatment of the salt with concentrated alkali. After separation of the salt, the ether solution yielded the vinylsulfondialkylamides.

Evidently, the reaction of amines with β-chloroethanesulfonyl chloride proceeds in three directions (I – III).

$$ClCH_2CH_2SO_2Cl + 2RNH_2 \rightarrow ClCH_2CH_2SO_2NHR + RNH_2HCl \quad (I)$$

$$ClCH_2CH_2SO_2NHR + RNH_2 \rightarrow CH_2{=}CHSO_2NHR + RNH_2HCl \quad (II)$$

$$CH_2{=}CHSO_2NHR + RNH_2 \rightarrow RNHCH_2CH_2SO_2NHR \quad (III)$$

On the basis of literature data and the results of the present investigation, it can be stated that reactions (I) and (II) proceed at a high rate. Due to the similarity of the rates of these reactions, it was not possible to obtain β-chloroethanesulfondialkylamides by this method. The rate of reaction (III) depends to a considerable extent on the character of the amine. Thus, aromatic amines add to vinylsulfonarylamides only on heating, while aliphatic amines add readily in the cold. Dialkylaminoethanesulfondialkylamides were also obtained in this investigation by the addition of dialkylamines to vinylsulfondialkylamides at room temperature.

EXPERIMENTAL

β-Chloroethanesulfonyl chloride was obtained by chlorination of di-β-chloroethyl disulfide in an aqueous medium at a temperature below 10° [5]. The yield was 83%.

Reaction of β-chloroethanesulfonyl chloride with dimethylamine. With stirring and cooling, a solution of 18.1 g of dimethylamine in 100 ml of ether was added over a period of 4 hours to a solution of 21.9 g of the

sulfonyl chloride in 150 ml of absolute ether while the temperature was kept at about -10°. After the addition of the amine, the temperature of the reaction mass was allowed to rise to room temperature, the precipitate removed, the ether evaporated from the filtrate and the residue fractionated in vacuum. We obtained 6.5 g (35.8%) of the dimethylamide of vinylsulfonic acid; b.p. 114 – 116° (13 mm) or 104 – 105° (8 mm), d_4^{19} 1.1655, n_D^{19} 1.4610.

Found %: N 10.56, 10.64. $C_4H_9O_2NS$. Calculated %: N 10.37.

If gaseous dimethylamine was passed through an ether solution of β-chloroethanesulonyl chloride, cooled with ice and salt, the main reaction product was dimethylaminoethanesulfondimethylamide. After removal of the precipitate formed during the reaction, dry hydrogen chloride was passed through the ether solution. The hydrochloride of dimethylaminoethansulfondimethylamide had m.p. 193° (from anhydrous alcohol).

Found %: Cl 16.16. $C_6H_{17}O_2N_2SCl$. Calculated %: Cl 16.40.

The free base was isolated by treatment of the hydrochloride with concentrated alkali. Dimethylaminoethanesulfondimethylamide boiled at 119 – 120° (15 mm) and crystallized at room temperature.

Found %: N 15.70, 15.82. $C_6H_{16}O_2N_2S$. Calculated %: N 15.56.

Reaction of β-chloroethanesulfonyl chloride with diethylamine. With stirring and cooling in ice and salt, 43 g of diethylamine was added over a period of an hour to a solution of 30.5 g of β-chloroethanesulfonyl chloride in 150 ml of dry chloroform (with the reaction temperature below 0°). The temperature was then allowed to rise slowly to room temperature. The chloroform solution was washed first with water, acidified with hydrochloric acid, and then with water and dried with sodium sulfate. After removal of the chloroform, fractional distillation gave 15.1 g of the diethylamide of vinylsulfonic acid with b.p. 110 – 111° (6 mm) or 114 – 116° (8 mm), d_4^{21} 1.1183, n_D^{22} 1.4631. The yield was 50% and did not depend on the dilution or the reaction temperature.

The diethylamide of vinylsulfonic acid readily added amines at the double bond. 1.2 g of diethylamine was added to 2.5 g of the diethylamide and after it had stood for some time, the mixture was vacuum distilled. We isolated two fractions: 1st 105 – 126° (1 mm), 2nd 126 – 131° (1 mm), 2g. The second fraction had an alkaline reaction. Dry hydrogen chloride was passed through an ether solution of the second fraction. The precipitate was separated and washed with ether. We obtained 1.7 g of a salt, which was readily soluble in water and alcohol and insoluble in ether; m.p. 120 – 122°. After solution in a small amount of alcohol and precipitation with absolute ether, the hydrochloride of diethylaminoethanesulfondiethylamide was obtained in the form of beautiful needles with m.p. 126 – 127°.

Found %: Cl 12.54, 12.46. $C_{10}H_{25}O_2N_2SCl$. Calculated %: Cl 13.03.

Treatment of the salt with concentrated alkali yielded diethylaminoethanesulfondiethylamide with b.p. 132 – 133° (1 mm), d_4^{24} 1.0249, n_D^{20} 1.4620.

Found %: N 11.76, 12.03. $C_{10}H_{24}O_2N_2S$. Calculated %: N 11.86.

SUMMARY

It was established that the action of dimethyl- and diethylamine on β-chloroethanesulfonyl chloride gave up to 50% yields of the dialkylamides of vinylsulfonic acid and dialkylaminoethanesulfondialkylamides.

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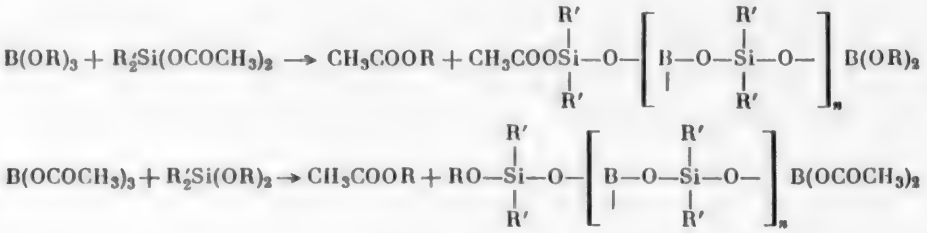
STUDY OF THE MECHANISM OF POLYORGANOBOROSILOXANE FORMATION WITH A HEAVY OXYGEN ISOTOPE

R. V. Kudryavtsev, D. N. Kursanov and K. A. Andrianov

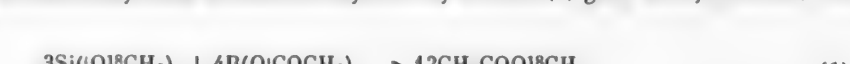
Institute of Organoelement Compounds, Academy of Sciences, USSR

In 1953 Wiberg et al. [1] prepared polyborosilicic esters. In 1955 Henglein and Lang [2] and in 1957 K. A. Andrianov and L. M. Volkova [3] studied this reaction and the properties of the polyorganoborosiloxanes formed. As starting materials it is possible to use either esters of boric acid and acetoxysilanes or triacetoxyboron and alkoxysilanes. In both cases polyorganoborosiloxanes are obtained during the reaction and an acetic ester liberated.



We set out to investigate the direction of rupture of the bonds during the formation of polyorganoborosiloxanes. For this purpose we prepared trimethyl borate and tetramethoxysilane with a high (compared with the natural one) concentration of the heavy isotope of oxygen, O^{18} (0.4 at.% excess of O^{18}).

The interaction of tetramethoxysilane with triacetoxyboron by scheme (1) gave methyl acetate, containing



(1)

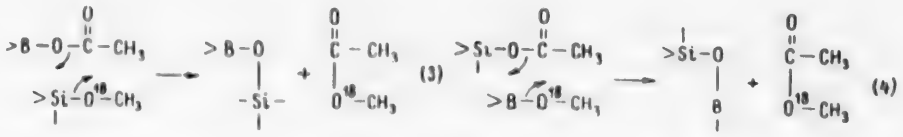
all the excess O^{18} from the tetramethoxysilane; consequently during the reaction there occurred rupture of the Si – O and O – C bonds [see dotted line in equation (1)]; the C – O bonds in the tetramethoxy silane and the B – O bonds in the triacetoxyboron were untouched (their rupture would have led to the formation of methyl acetate without excess O^{18}).

It might have been expected that in the interaction of trimethyl borate and diethyldiacetoxysilane by scheme (2)

(2)

there would also have been rupture of the C – O bond in the boric acid derivative and rupture of the Si – O bond in the organosilicon component. In this case, the methyl acetate obtained would not have contained excess of the heavy isotope of oxygen. However, in actual fact it was found that the methyl acetate contained the whole of the excess O^{18} from the trimethyl borate and hence it follows that rupture of the B – O and O – C bonds [see dotted line in scheme (2)] occurred.

The results obtained may be explained in two ways. It is possible that both the reaction of tetramethoxysilane and triacetoxyboron and the reaction of trimethyl borate and diethyldiacetoxysilane proceeded by cyclic mechanisms (3) and (4).



(3)

(4)

However, it is practically impossible to carry out the reaction under absolutely anhydrous conditions and if traces of moisture were present in the original components or in the reaction system, then hydrolysis of one of the original components would occur. This would liberate methyl alcohol, $CH_3O^{18}H$ or acetic acid, which in their turn would produce alcoholysis [4] or acidolysis of the other original component and the formation of methyl acetate. Thus, the process represented in equation (1) could include the group of reactions (5).

$$
\left.\begin{array}{l}
B(OCOCH_3)_3 + H_2O \longrightarrow HOB(OCOCH_3)_2 + CH_3COOH \\
Si(O^{18}CH_3)_4 + CH_3COOH \longrightarrow CH_3COO^{18}CH_3 + HOSi(O^{18}CH_3)_3 \\
2HOSi(O^{18}CH_3)_3 \longrightarrow (CH_3O^{18})_3Si{-}O{-}Si(O^{18}CH_3)_3 + H_2O \\
Si(O^{18}CH_3)_4 + HOB(OCOCH_3)_2 \longrightarrow (CH_3O^{18})_3Si{-}O{-}B(OCOCH_3)_2 + CH_3O^{18}H \\
Si(O^{18}CH_3)_4 + H_2O \longrightarrow (CH_3O^{18})_3Si{-}OH + CH_3O^{18}H \\
B(OCOCH_3)_3 + CH_3O^{18}H \longrightarrow CH_3COO^{18}CH_3 + HOB(OCOCH_3)_2 \\
B(OCOCH_3)_3 + 3CH_3O^{18}H \longrightarrow B(O^{18}CH_3)_3 + 3CH_3COOH, \text{ etc.}
\end{array}\right\} \quad (5)
$$

The process represented in equation (2) could include the group of reactions (6).

$$
\left.\begin{array}{l}
B(O^{18}CH_3)_3 + H_2O \longrightarrow HOB(OCH_3)_2 + CH_3O^{18}H \\
(C_2H_5)_2Si(OCOCH_3)_2 + CH_3O^{18}H \longrightarrow CH_3COO^{18}CH_3 + (C_2H_5)_2Si(OH)(OCOCH_3) \\
(C_2H_5)_2Si(OH)(OCOCH_3) \longrightarrow [(C_2H_5)_2(CH_3COO)Si]_2O + H_2O \\
(C_2H_5)_2Si(OCOCH_3)_2 + H_2O \longrightarrow CH_3COOH + (C_2H_5)_2Si(OCOCH_3)(OH) \\
B(O^{18}CH_3)_3 + CH_3COOH \longrightarrow CH_3COO^{18}CH_3 + HOB(O^{18}CH_3)_2, \text{ etc.}
\end{array}\right\} \quad (6)
$$

What equations (3) – (6) have in common is that in all cases the $O^{18} - CH_3$ bond is retained and the formation of $CH_3COO^{18}CH_3$ proceeds with rupture of the $B - O^{18}CH_3$ or $Si - O^{18}CH_3$ bonds on the one hand and the $SiO - COCH_3$ or $BO - COCH_3$ bonds on the other.

EXPERIMENTAL

Preparation of $CH_3O^{18}H$ (I). 40 g of sodium was dissolved in anhydrous methyl alcohol and then 120 ml of H_2O^{18} (containing 1.5 at.% O^{18}) was added and practically the whole of the methyl alcohol distilled off on a column. To the solution of $NaO^{18}H$ in H_2O^{18} was added 197 g of dimethyl sulfate with heating. The (I) obtained was distilled off as it formed. We obtained 85 ml of (I) with b.p. 64°, n_D^{20} 1.3318, and containing 0.6 at.% of O^{18}.

Preparation of $Si(O^{18}CH_3)_4$ (II). 18 g of (I) was added dropwise with stirring to 22.4 g of silicon tetrachloride, cooled with dry ice. After the addition of the whole of (I), the mixture was cooled for a further 15 – 20minutes, then cooling was stopped and dry air passed through the flask. When the evolution of hydrogen chloride ceased, the mixture was distilled. We obtained 7.6 g of (II) with n_D^{20} 1.3679, and b.p. 121 – 122°.

Interaction of (II) with triacetoxyboron. To 1.72 g of triacetoxyboron [5] was added 2.38 g of (II) and the mixture heated. At 90° a homogeneous mixture was formed. The methyl acetate formed was removed by distillation. We obtained 3 g of methyl acetate with b.p. 57° and n_D^{20} 1.3600. This methyl acetate was contaminated by an insignificant amount of trimethyl borate and to remove this, water was added dropwise until the formation of a precipitate of H_3BO_3 ceased. The excess water was removed by the addition of fired magnesium sulfate and the mixture distilled to remove the boric acid. After this, anhydrous methylene chloride was added and

the azeotrope of methylene chloride with methyl alcohol distilled at 39°; methylene chloride then distilled at 41° and methyl acetate (n_D^{20} 1.3595) at 57°. Isotope analysis of the methyl acetate obtained in this way showed that it contained 0.39 at.% of O^{18}, which corresponds to 0.58 at.% in the ester oxygen.

Preparation of $B(O^{18}CH_3)_3$ (III). 5 g of finely ground boric anhydride was added with stirring to 16 g of (I) [6]. On the following day the solution was decanted and the azeotrope of (III) with methyl alcohol distilled at 54 – 60°. To the azeotropic mixture (11.1 g) was added 1.3 g of anhydrous lithium chloride. The solution of lithium chloride in methyl alcohol was separated [7] and then 3.56 g of (III) distilled at 67.6 – 67.9°. The unreacted (I) was practically completely recovered.

Interaction of (III) with diethyldiacetoxysilane. 12.4 g of diethyldiacetoxysilane [4] was added to 3.56 g of (III). The reaction mixture was boiled in the flask of a column with an efficiency of 17 theoretical plates. The temperature of the vapor at first equalled 67.5°. After 15 – 20 minutes the temperature fell to 56.5° and 7.7 ml of methyl acetate was distilled. The methyl acetate was freed from traces of trimethyl borate as described above. The methyl acetate obtained had b.p. 57° and n_D^{20} 1.3672 and contained traces of methylene chloride. Isotope analysis of the methyl acetate showed that it contained 0.38 at.% of O^{18}, which corresponds to 0.56 at.% in the ester oxygen.

SUMMARY

1. By means of a heavy isotope of oxygen, a study was made of the interaction of tetramethoxysilane with triacetoxyboron and of trimethyl borate with diethyldiacetoxysilane. It was shown that in both cases the $O-CH_3$ bond was retained and the formation of methyl acetate proceeded with rupture of the $B-OCH_3$ or the $Si-OCH_3$ bonds, on the one hand, and the $SiO-COCH_3$ or $BO-COCH_3$ bonds, on the other.

2. Trimethyl borate-O^{18} and tetramethoxysilane-O^{18} were synthesized.

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ACYLATION OF ARYLALIPHATIC DISILOXANES. SYNTHESIS OF BIS-(4, 4'-ACETOBENZYL)-TETRAMETHYLDISILOXANE

K. A. Andrianov, V. A. Odinets and A. A. Zhdanov

Institute of Organoelement Compounds, Academy of Sciences, USSR

The Friedel-Crafts reaction is of limited application in silicoorganic chemistry since silicoorganic compounds containing a phenyl radical connected to a silicon atom usually decompose under the action of acid catalysts with the elimination of the aromatic nucleus [1, 2]. Only a few examples are known of the acylation of an aromatic nucleus, connected to silicon, with acetyl fluoride in the presence of boron triflouride [3]; toluene has been acylated by m- and p-trimethylsilylbenzoyl chlorides [1]. The alkylation of benzene by chloromethylmethylchlorosilanes in the presence of aluminum chloride has been described in the literature [4]. By this method it is possible to obtain benzylmethylchlorosilanes or benzyltrimethylsilanes in which the aromatic nucleus is connected to the silicon atom through a methylene group. In the literature there is also a description of the acylation of benzyltrimethylsilane [5], proceeding by the scheme:

$$(CH_3)_3SiCH_2C_6H_5 + CH_3COCl \xrightarrow{AlCl_3} (CH_3)_3SiCH_2C_6H_4COCH_3 + HCl.$$

According to this equation, acetobenzyltrimethylsilane was obtained in 41% yield.

The formation of benzylmethylchlorosilanes and the acylation of benzyltrimethylsilane indicates that the Friedel-Crafts reactions may be used successfully for the synthesis of various derivatives of benzylsiloxanes, in which the aromatic nucleus is separated from the silicon atom by a methylene group. As our investigations showed, benzyldimethylchlorosilane is not decomposed in the presence of aluminum chloride and may be used successfully as the starting material for the synthesis of bis-(acetobenzyl)-tetramethyldisiloxane.

We obtained the benzyldimethylchlorosilane by a Grignard reaction from dimethyldichlorosilane and benzylmagnesium chloride according to the reaction:

$$(CH_3)_2SiCl_2 + C_6H_5CH_2MgCl \longrightarrow (CH_3)_2C_6H_5CH_2SiCl + MgCl_2.$$

For isolation of the pure product, after the organomagnesium synthesis, the reaction mixture was hydrolyzed with water and the impure dibenzyltetramethyldisiloxane, formed as a result of hydrolysis, was converted into the chloride by treatment with sulfuric acid and ammonium chloride by the reaction:

$$2(CH_3)_2C_6H_5CH_2SiCl + H_2O \longrightarrow (CH_3)_2C_6H_5CH_2SiOSiCH_2C_6H_5(CH_3)_2 + 2HCl$$
$$(CH_3)_2C_6H_5CH_2SiOSiCH_2C_6H_5(CH_3)_2 + 2NH_4Cl + 2H_2SO_4 \longrightarrow$$
$$\longrightarrow 2(CH_3)_2C_6H_5CH_2SiCl + NH_4HSO_4 + H_2O.$$

The acylation of benzyldimethylchlorosilane was accomplished according to the following equation.

$$(CH_3)_2C_6H_5CH_2SiCl + (CH_3CO)_2O + AlCl_3 \longrightarrow$$
$$\longrightarrow CH_3COC_6H_4CH_2(CH_3)_2SiCl + CH_3COOAlCl_2 + HCl \xrightarrow{H_2O}$$
$$\longrightarrow CH_3COC_6H_4CH_2(CH_3)_2SiOSi(CH_3)_2CH_2C_6H_4COCH_3$$

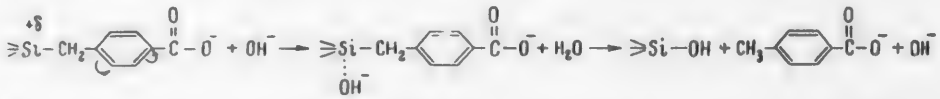
The bis-(acetobenzyl)-tetramethyldisiloxane we synthesized had the properties of aliphatic-aromatic ketones and formed a dinitrophenylhydrazone, with the reaction occurring at both carbonyl groups.

$$2(NO_2)_2C_6H_3NHNH_2 + CH_3COC_6H_4CH_2(CH_3)_2SiOSi(CH_3)_2CH_2C_6H_4COCH_3 \longrightarrow$$
$$\longrightarrow [(NO_2)_2C_6H_3NHN{=}C(CH_3)C_6H_4CH_2(CH_3)_2Si]_2O + 2H_2O$$

Oxidation of bis-(acetobenzyl)-tetramethyldisiloxane with sodium hypobromite in an alkaline medium gave p-toluic acid, which we identified as the methyl ester.

$$CH_3COC_6H_4CH_2(CH_3)_2SiOSi(CH_3)_2CH_2C_6H_4COCH_3 + 6NaBrO + H_2O \longrightarrow$$
$$\longrightarrow 2CHBr_3 + 4NaOH + 2CH_3C_6H_4COONa + [Si(CH_3)_2O]_x$$

The comparatively ready elimination of the benzylcarboxy group is connected with transfer of the reactivity by the system of conjugated bonds of the nucleus, as a result of which there is a reduction in the electron density at the silicon atom and subsequent rupture of the Si – C bond under the action of a nucleophilic agent.



With the use of an alkaline solution of potassium permanganate as the oxidant, the oxidation proceeds completely with the formation of terephthalic acid. The formation of p-toluic and terephthalic acids indicates that the aceto group enters the position para to the methylene group in the Friedel-Crafts reaction. The properties of the compounds synthesized are presented in the table.

EXPERIMENTAL

Starting materials: the dimethyldichlorosilane had b.p. 70° (chlorine content 55.0%), the benzyl chloride had b.p. 178 – 180°-and the aluminum chloride was anhydrous and unsublimed.

Benzylation of dimethyldichlorosilane. Into a flask, fitted with a stirrer, a thermometer, a dropping funnel and a reflux condenser, was placed 12 g of magnesium and 50 ml of ether. The mixture was heated to 30° and a solution of 63.2 g of benzyl chloride in 100 ml of ether run into the flask dropwise. The reaction usually began 3 – 5 minutes after the introduction of the mixture. During the reaction, the temperature was kept at about 35°. After the introduction of the benzyl chloride, the mixture was stirred for a further 2 hours and then the solution of Grignard reagent was decanted from the unreacted magnesium. Into a reaction flask was placed 64.9 g of dimethyldichlorosilane in 100 ml of ether and with vigorous stirring and cooling, the Grignard reagent obtained was introduced from a dropping funnel. When the reaction was complete, the mixture was stirred for 4 hours at 35° and then cooled.

Hydrolysis of benzylation products. Into a separatory funnel was placed 400 ml of 5% hydrochloric acid and a small amount of ice; with vigorous stirring, the reaction mixture obtained in the previous experiment was introduced into the funnel. When the hydrolysis was complete, the ether layer was separated from the aqueous one; the latter was extracted once with ether and the combined ether solutions were washed with water and dried with sodium sulfate. Removal of the ether yielded 70 g of a liquid product, containing impure dibenzyltetramethyldisiloxane.

Benzyldimethylchlorosilane. Into a flask were placed 35.7 g of ammonium chloride and 70 g of dibenzyltetramethyldisiloxane, obtained in the previous experiment. With stirring and cooling in ice, 87.3 g of sulfuric acid (d 1.84) was slowly added to the mixture. During the whole introduction of the sulfuric acid, the temperature in the reaction mixture was kept at not higher than 4°. The mixture was then stirred for a further 15 – 20 minutes and the liquid decanted from the ammonium sulfate and separated from the lower sulfuric acid layer. The reaction product was vacuum distilled. We obtained 36.8 g of benzyldimethylchlorosilane:

b.p. 72 – 73° (7 mm), d_4^{20} 1.0159, n_D^{20} 1.5090, MR 54.29; Calc. 54.18.

Substance	Temperature		d_4^{20}	nD^{20}	MR_D		Empirical formula	%C		%H		%Si		%Cl	
	boiling point (pressure in mm)	melting point			found	calc.		found	calc.	found	calc.	found	calc.	found	calc.
Benzyldimethylchlorosilane $C_6H_5CH_2(CH_3)_2SiCl$	72-73° (7)	—	1.0159	1.5090	54.29	54.18	$C_9H_{13}SiCl$	58.40, 58.23	58.51	7.52, 7.35	7.09	14.37, 14.69	15.17	19.55, 19.28	19.19
Bis-(acetobenzyl)-tetramethyl-disiloxane $[CH_3COC_6H_4CH_2-(CH_3)_2Si]_2O$	260-261 (5)	63°	—	—	—	—	$C_{22}H_{30}O_3Si_2$	66.04, 65.81	66.29	7.65, 7.69	7.59	14.11, 14.27	14.08	—	—
2,4-Dinitrophenylhydrazone of bis-(acetobenzyl)-tetramethyl-disiloxane $[(NO_2)_2C_6H_3NHN=C(CH_3)C_6H_4CH_2(CH_3)_2Si]_2O$	—	259-260	—	—	—	—	$C_{34}H_{38}O_9N_8Si_2$	53.94, 54.17	53.82	5.17, 5.19	5.05	8.05, 8.03	7.39	N14.01, 13.92	N 14.77

Found %: C 58.40, 58.23; H 7.52, 7.35; Cl 19.55, 19.28; Si 14.37, 14.69. $C_9H_{13}SiCl$. Calculated %: C 58.51; H 7.09; Cl 19.19; Si 15.17.

Bis-(acetobenzyl)-tetramethyldisiloxane. Into a flask were placed 26.6 g of aluminum chloride, 18.5 g of benzyldimethylchlorosilane and 30 ml of petroleum ether. With stirring, 10.2 g of acetic anhydride was introduced into the mixture. During this, the temperature was kept at 18 – 20°. The mixture was then stirred for a further 2 hours at 50 – 55° and the reaction product hydrolyzed with 20% hydrochloric acid. The organic layer was separated from the aqueous one, washed until neutral, dried with sodium sulfate and after removal of the solvent, the residue fractionated in vacuum. We obtained 9.9 g of bis-(acetobenzyl)-tetramethydisiloxane with b.p. 260 – 261° (5 mm) and m.p. 63°. The yield was 50%.

Found %: C 66.04, 65.81; H 7.65, 7.69; Si 14.11, 14.27. $C_{22}H_{30}O_3Si_2$. Calculated %: C 66.29; H 7.59; Si 14.08.

The 2, 4-dinitrophenylhydrazone of bis-(acetobenzyl)-tetramethyldisiloxane was obtained by a known procedure [6] by heating a mixture of solutions of 1.98 g of dinitrophenylhydrazine in 3 ml of concentrated sulfuric acid and 15 ml of anhydrous alcohol and 2 g of bis-(acetobenzyl)-tetramethyldisiloxane in 5 ml of anhydrous alcohol. After recrystallization from a mixture of alcohol and toluene (1 : 1), the product had m.p. 259 – 260°.

Found %: C 53.94, 54.17; H 5.17, 5.19; Si 8.05, 8.03; N 14.01, 13.92. $C_{34}H_{38}O_5N_8Si_2$. Calculated %: C 53.81; H 5.05; Si 7.39; N 14.77.

Oxidation of bis-(acetobenzyl)-tetramethyldisiloxane with sodium hypobromite. Into a flask was placed 33 ml of water and 6.3 g of sodium hydroxide and with cooling, 2.5 ml of bromine was added to the solution. The solution of sodium hypobromite prepared was added in small portions to a separately prepared solution of 4 g of bis-(acetobenzyl)-tetramethyldisiloxane in 25 ml of dioxane. During the oxidation, the temperature rose to 30°. The mixture was stirred for 2 hours at 40° and about 15 ml of a saturated solution of sodium bisulfite added to decompose the excess hypobromite in the mixture. The mixture was then diluted with water to dissolve the precipitated salt and the bromoform was distilled off with a small amount of water. After filtration, the solution was acidified with hydrochloric acid and the precipitate of toluic acid was washed and recrystallized from aqueous alcohol. The m.p. was 179°.

The methyl ester of toluic acid was obtained by heating toluic acid with a 10-fold excess of methyl alcohol in the presence of 5% of sulfuric acid. Distillation yielded a fraction boiling at 85 – 87° (7 mm), which crystallized on standing. The m.p. was 33°.

Found %: C 71.72, 71.62; H 6.23, 6.37. $C_9H_{10}O_2$. Calculated %: C 71.90; H 6.57.

Oxidation of bis-(acetobenzyl)-tetramethyldisiloxane with potassium permanganate. A mixture of 4 g of bis-(acetobenzyl)-tetramethyldisiloxane, 7.5 g of potassium permanganate and 50 ml of a 10% solution of sodium hydroxide was heated with stirring for 12 hours at 80°. The mixture was then diluted with water, the excess permanganate decomposed with alcohol and the solution acidified after filtration. The terephthalic acid precipitated was washed with water, dried and purified by reprecipitation from an alkaline solution.

Found %: C 57.63, 57.48; H 3.81, 3.70. $C_8H_6O_4$. Calculated %: C 57.83; H 3.61.

The dimethyl ester of terephthalic acid had m.p. 139 — 140°.

SUMMARY

Benzyldimethylchlorosilane was synthesized and it was shown that the aromatic nucleus could be acetylated with acetic anhydride in the presence of aluminum chloride. Hydrolysis of the reaction mixture yielded bis-(acetobenzyl)-tetramethyldisiloxane. Oxidation of the latter with sodium hypobromite in an alkaline medium formed p-toluic acid.

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COHYDROLYSIS OF DIETHYLDICHLOROSILANE AND PHENYLTRICHLOROSILANE

K. A. Andrianov, D. Ya. Zhinkin and A. G. Kuznetsova

The main stage in the preparation of polyorganosiloxane resins is the cohydrolysis of alkyl- and arylchlorosilanes or alkyl- and arylethoxysilanes. Work [1 – 3] devoted to a study of the hydrolysis of difunctional and trifunctional organosilicon monomers, however, does not consider the problem of the cohydrolysis of monomers with different numbers of functional groups.

In the present article we present the results of a study of the cohydrolysis of equimolecular mixtures of diethyldichlorosilane with phenyltrichlorosilane. The process may proceed in two competing directions (1 and 2).

$$n(C_2H_5)_2SiCl_2 + nC_6H_5SiCl_3 + 2.5nH_2O \longrightarrow [(C_2H_5)_2SiO]_n + [C_6H_5SiO_{1.5}]_n + 5nHCl \quad (1)$$

$$n(C_2H_5)_2SiCl_2 + nC_6H_5SiCl_3 + 2.5nH_2O \longrightarrow [(C_2H_5)_2SiO(C_6H_5)SiO_{1.5}]_n + 5nHCl \quad (2)$$

The reaction proceeding by scheme (1) would give a mixture of polymeric products of the separate hydrolysis of diethyldichlorosilane and phenyltrichlorosilane, namely, polydiethylsiloxanes and polyphenylsiloxanes. If the hydrolysis were to proceed by scheme (2), it would give cohydrolysis products, polydiethylphenylsiloxanes. There is also the possibility of the formation of partial condensation products, containing hydroxyl groups.

To determine the direction of the reaction, an investigation was made of the hydrolysis products obtained by cohydrolysis of the monomers indicated above. To evaluate the results obtained, we compared analysis data with values calculated for the separate types of polymers, which could be obtained by hydrolysis of the mixture of monomers examined (Table 1).

TABLE 1

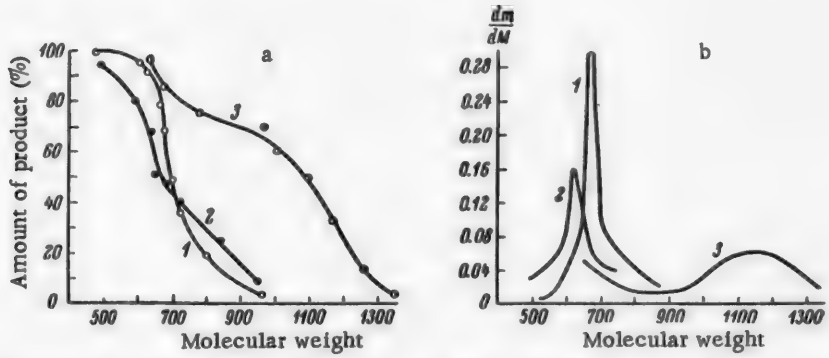
Calculated Characteristics of the Hydrolysis Products of an Equimolecular Mixture of Diethyldichlorosilane and Phenyltrichlorosilane

Hydrolysis products	Molecular weight of elementary unit	Content (in %)	
		silicon	OH groups
Polydiethylsiloxanes $[(C_2H_5)_2SiO]_n$	102	27.45	-
Polyphenylsiloxanes $[C_6H_5SiO_{1.5}]_n$	129	21.71	-
Polyphenylhydroxysiloxanes $[C_6H_5SiO(OH)]_n$	138	20.29	12.31
Polydiethylphenylsiloxanes $[(C_2H_5)_2SiO(C_6H_5)SiO_{1.5}]_n$	231	24.24	-
Polydiethylphenylhydroxysiloxanes $[(C_2H_5)_2SiO(C_6H_5)SiO(OH)]_n$	240	23.33	7.08

By hydrolysis of an equimolecular mixture of diethyldichlorosilane and phenyltrichlorosilane with excess water in an ether medium, we obtained hydrolysis products, which were separated into eleven fractions by fractional precipitation from a solution in acetone. The silicon content of the different fractions of hydrolysis products was 23.5 – 24.02% and the hydroxyl group content, 2.11 – 2.88%.

Carrying out the hydrolysis under the same conditions, but with acetone present as a solvent, and subsequent fractionation of the hydrolysis products gave products with a silicon content of 23.7 – 24% and 2.37 – 4.03% of hydroxyl groups.

Analysis of ten fractions, obtained by fractional precipitation of the products from hydrolysis of a mixture of diethyldichlorosilane and phenyltrichlorosilane in the presence of benzene, showed that the silicon content varied over the range 23.67 – 24.12% with a hydroxyl group content of 0.93 – 2.7%. Thus, the hydrolysis products, obtained in ether, acetone and benzene media, could be considered as consisting of mixtures of polydiethylphenylsiloxanes and polydiethylphenylhydroxysiloxanes.



Molecular weight distribution curves (a) and differential molecular weight distibution curves (b) of cohydrolysis products of $(C_2H_5)_2SiCl_2$ and $C_6H_5SiCl_3$. Hydrolysis solvent: 1) ether, 2) acetone, 3) benzene.

Determination of the average molecular weights of fractions of the cohydrolysis products showed that depending on the solvent used, the value of the molecular weights and the dispersion of the cohydrolysis product changed considerably. The molecular weight distribution curves (a) of the cohydrolysis product for each of the solvents investigated and also the differential distribution curves (b) are presented in the figure. The figure shows that the value of the molecular weights of the separate fractions, constituting the cohydrolysis products obtained in different solvents, corresponds to the range 490 – 970 for ether, 490 – 950 for acetone and 670 – 1350 for benzene. Thus, the cohydrolysis products in benzene have a greater dispersion than where ether and acetone were used.

If we examine the differential distribution curve of the cohydrolysis products, obtained in an ether medium, then a characteristic maximum is observed in the region corresponding to molecular weights of 650 – 700. This fraction represented about 40% of the total polymer weight.

The distribution curve of the cohydrolysis products obtained in an acetone medium has a maximum in the region of 600 – 660. The fraction corresponding to these molecular weights represented about 27% of the total cohydrolysis products.

The distribution curve of the cohydrolysis products obtained in a benzene medium has two characteristic sections: there is a maximum in the molecular weight region of 1100 – 1200 (about 23% of the total polymers) and a marked maximum in the region of 600 – 650.

If we consider that the basic structural units of the copolymer, $(C_2H_5)_2SiO(C_6H_5)SiO_{1.5}$ and $(C_2H_5)_2SiO$-$(C_6H_5)_2SiO(OH)$, have molecular weights of 231 and 240, respectively, then there are grounds for considering that the cohydrolysis products obtained in ether consist predominantly of polymers containing 6 atoms of silicon

TABLE 2

Values of Coefficients in the Formula For the Composition of the Hydrolysis Product

Solvent	Value of (m + n)			Value of (m : n)		
	max.	min.	average	max.	min.	average
Ether	4	2	3.25	0.8	0.6	0.68
Acetone . . .	4	2	3.0	1.12	0.66	0.78
Benzene . . .	6	3	4.94	0.75	0.26	0.48

in the molecule. To a certain extent, the same is also correct for products obtained in an acetone medium. The cohydrolysis products obtained in benzene also contain a considerable amount of a fraction with 6 atoms of silicon in the molecule. In addition, the second maximum, lying in the molecular weight region of 1100 - - 1200, corresponds closely to polymers, whose molecules contain 12 silicon atoms.

The results of investigating the cohydrolysis products of diethyldichlorosilane and phenyltrichlorosilane with excess water indicate that the composition of the mixture of polymers formed during the hydrolysis may be expressed by the formula

$$[(C_2H_5)_2SiOC_6H_5SiO(OH)]_m[(C_2H_5)_2SiOC_6H_5SiO_{1.5}]_n,$$

where (m + n) is the degree of polymerization and (m : n) is the ratio between the polydiethylphenylhydroxy- and the polydiethylphenylsiloxanes. The average values of these coefficients for the different experimental conditions are presented in Table 2.

As the data in Table 2 show, the solvent has an effect not only on the dispersion of the mixture of copolymers and the degree of polymerization, but also on the amount of hydroxyl-containing compounds (products of incomplete condensation) in the hydrolysis product. The hydrolysis products obtained in an ether medium had the greatest hydroxyl group content and those obtained in a benzene medium, the least.

EXPERIMENTAL

Starting materials. Phenyltrichlorosilane was isolated by distillation of the technical product. In the distillation, we collected a fraction with b.p. 200 – 202° (chlorine content 50.7%; calculated, 50.35%). The diethyldichlorosilane was obtained by fractionation of the technical product on a column with an efficiency of 20 theoretical plates. The b.p. was 127° (chlorine content 44.94%; calculated, 45.22%).

Hydrolysis of a mixture of diethyldichlorosilane and phenyltrichlorosilane. Into a four-necked flask, fitted with a stirrer with a mercury seal, a thermometer, a reflux condenser and a dropping funnel and cooled with a mixture of ice and salt, was poured 300 g of water and 180 g of solvent. The solvents used were ether, benzene and acetone. Over a period of 0.5 – 1 hour, a mixture of 78.5 g of diethyldichlorosilane and 105.3 g of phenyltrichlorosilane was introduced into the flask from a dropping funnel with stirring and at a temperature of not more than 35°. The contents of the flask were then stirred for 1 hour at the same temperature. The acid solution of the hydrolysis products was separated in a separating funnel and washed with 150 ml portions of water until no longer acid to congo (2 – 3 washings). The solution was dried over sodium sulfate for 10 – 12 hours and filtered. When the solvent had been evaporated at 30° in vacuum, the involatile content of the hydrolysis products was determined by drying in a thermostat at 150° for 3 hours.

Fractionation of hydrolysis products. 40 – 50 g of the hydrolysis product (calculated on 100%) was dissolved in a sufficient amount of acetone to give a 3% solution (1.7 – 2.1 liters). The solution of hydrolysis products was placed in a 4 – 5 liter round-bottomed flask. Water was gradually introduced from a buret into the flask with the solution with continuous stirring until a stable turbidity was formed in the solution. The solution was heated on a water bath at about 50°; on heating, the solution became clear. On standing at 20 – 25° for 12 – 100 hours, the solution deposited a viscous liquid at the bottom of the flask. This liquid was collected from the bottom of the flask with a pipette, separated from the solution in a separatory funnel, dissolved in acetone and filtered through a paper filter. The solution obtained in this way was placed in a glass vessel in a vacuum desiccator (about 20 mm residual pressure) to evaporate the solvent. By precipitation, we isolated 10 – 11 fractions weighing 1 – 6 g.

Analysis of fractions. Silicon was determined by oxidation of a sample in a quartz flask with a mixture of oleum and concentrated nitric acid, containing oxides of nitrogen. The residue after oxidation was fired in a muffle at 800° to constant weight. The hydroxyl group content was determined by the Tserevitinov-Terent'ev method. The molecular weight was measured cryoscopically in benzene and dioxane.

SUMMARY

Hydrolysis of an equimolecular mixture of diethyldichlorosilane and phenyltrichlorosilane with excess water in an acid medium in the presence of solvent formed cohydrolysis products corresponding to the formula

$$[(C_2H_5)_2SiOC_6H_5SiO(OH)]_m[(C_2H_5)_2SiOC_6H_5SiO_{1.5}]_n.$$

The dispersion of the mixture of copolymers and also the content of hydroxyl derivatives in the hydrolysis products varied, depending on the character of the solvent used in the hydrolysis.

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POLYDIETHYLSILOXANE LIQUIDS

III. ACTION OF CARBOXYLIC ACIDS ON DIETHYLDIETHOXYSILANE

N. S. Leznov, L. A. Sabun and K. A. Andrianov

In previous communications [1, 2] it was shown that the action of mineral acids on diethyldiethoxysilane formed ethyl esters of the corresponding acids and polydiethylsiloxanes. The chemical and fractional composition of the latter dpended on the nature of the acid, its concentration, the quantitative ratios of the reagents and the reaction conditions.

In the present communication we present data on the reactions of diethyldiethoxysilane with mono- and dicarboxylic acids. The investigation carried out showed that heating monocarboxylic acids (formic, acetic, chloroacetic, propionic and n-butyric) with diethyldiethoxysilane to 66 – 120° led to the formation of polydiethylsiloxanes in up to 98% yield according to scheme (I).

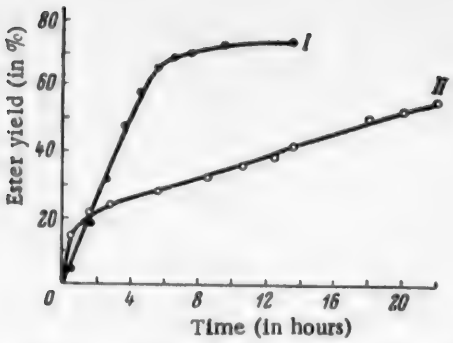
$$(C_2H_5)_2Si(OC_2H_5)_2 \xrightarrow[-2RCOOC_2H_5;\ -H_2O]{2RCOOH} \rightarrow [(C_2H_5)_2SiO]_x + (C_2H_5)_2Si(OC_2H_5)-O-\left[Si(C_2H_5)_2-O\right]_{x'}-Si(C_2H_5)_2(OC_2H_5) \quad (I)$$

(a) (b)

Cyclic polydiethylsiloxanes (a), free from linear polymers containing ethoxy groups in the molecule (b), could be obtained if more acid than the amount calculated from scheme (I) was used in the reaction. The excess depended on the concentration of the acid and its dissociation constant and decreased with an increase in the latter (Table 1).

TABLE 1

Acid		Reaction temperature	Duration (in hours)	Excess of acid (in %)	Ethoxy group content of polydiethylsiloxanes (in %)
Chloroacetic		95-100°	1	0	0
Formic	(99.4%)	65- 68	3	10	0
	(85%)	65- 68	6	10	2.43
	(85%)	65- 68	5	25	0
Acetic	(100%)	88-90	6	25	0
	(80%)	88-90	12	37.5	0.11



Kinetics of ethyl acetate (I) and ethyl n-butyrate (II) formation in the reaction of the corresponding acids with diethyldiethoxysilane.

With an insufficient excess of the acid, it was not possible to obtain polydiethylsiloxanes free from traces of linear polymers containing ethoxy groups in the molecule by increasing the reaction time.

The given effect of concentration and acid strength in the reactions of carboxylic acids with diethyldiethoxysilane is explained in the following way. In accordance with scheme (I), water is liberated during the reaction and as it accumulates the hydrolysis of diethyldiethoxysilane proceeds with the formation of diethyldihydroxysilane and diethylhydroxyethoxysilane by scheme (II).

Diethylhydroxyethoxysilane hinders cyclization of diethyldihydroxysilane after its dehydration by saturating the terminal units of the polymer formed with diethylethoxysilyl groups according to scheme (III).

$$(C_2H_5)_2Si(OC_2H_5)_2 + H_2O \xrightarrow{-C_2H_5OH} (C_2H_5)_2Si\begin{matrix}OH\\OH\end{matrix} + (C_2H_5)_2Si\begin{matrix}OC_2H_5\\OH\end{matrix} \qquad (II)$$

$$(C_2H_5)_2Si\begin{matrix}OH\\OH\end{matrix} \xrightarrow{-H_2O} \left[(C_2H_5)_2Si{-}O{-}\right] \xrightarrow{(C_2H_5)_2Si\begin{matrix}OC_2H_5\\OH\end{matrix}}$$

$$\rightarrow (C_2H_5)_2Si(OH){-}O{-}\left[Si(C_2H_5)_2{-}O\right]_x{-}Si(C_2H_5)_2(OC_2H_5) \xrightarrow{-H_2O}$$

$$\rightarrow (C_2H_5)_2Si(OC_2H_5){-}O{-}\left[Si(C_2H_5)_2{-}O\right]_{x'}{-}Si(C_2H_5)_2(OC_2H_5) \qquad (III)$$

Apparently, due to the low concentration of these groups and the hydrophobic nature of the polymeric compound, hydrolysis of the ethoxy groups in the polymers requires more drastic action than that of the aqueous solution of acid remaining at the end of the reaction, which is naturally weaker, the less the excess of acid and the lower its concentration.

The rate of the reaction of carboxylic acids with diethyldiethoxysilane also depends on the strength of the acid and increases with an increase in the latter (Figure).

It was established that the introduction of 0.1 – 0.2% of sulfuric acid into the reaction mixture led to a sharp increase in the reaction rate; here the difference in the time of the process, depending on the strength of the carboxylic acid, was reduced to a minimum. Simultaneously with this, the introduction of the given catalyst made it possible to reduce the required excess of acid for preventing the formation of polymers containing ethoxy groups in the molecule.

Experimental data obtained previously in an investigation of the reaction of diethyldiethoxysilane with mineral acids makes it possible to explain the catalytic effect of sulfuric acid not only by its known action in esterification reactions, which occurs in the case considered (scheme II), but also by direct interaction with diethyldiethoxysilane, which proceeds at a high rate at room temperature according to scheme (IV).

$$(C_2H_5)_2Si(OC_2H_5)_2 + 2H_2SO_4 \rightarrow [(C_2H_5)_2SiO]_x + 2C_2H_5OSO_3H + H_2O \qquad (IV)$$

Regeneration of sulfuric acid on esterification of the carboxylic acid, occurring in the reaction mixture, makes it possible to realize the process in scheme (IV) with a very small amount of it with the concentration of the carboxylic acid at a suitable level. The experimental data also showed that the action of acetic acid on diethyldiethoxysilane with continuous removal of the volatile substances from the reaction mixture with benzene vapor did not lead to the formation of polydiethylsiloxanes and ethyl acetate, but caused the formation of diethyldiacetoxysilane by scheme (V).

$$(C_2H_5)_2Si(OC_2H_5) + 2CH_3COOH \longrightarrow (C_2H_5)_2Si\begin{matrix}OCOCH_3\\OCOCH_3\end{matrix} + 2C_2H_5OH \qquad (V)$$

When heated with diethyldiethoxysilane in the presence of traces of sulfuric or ethyl sulfuric acids, diethyldiacetoxysilane was readily converted into cyclic polydiethylsiloxanes and ethyl acetate by scheme (VI).

$$(C_2H_5)_2Si(OCOCH_3)_2 + (C_2H_5O)_2Si(C_2H_5)_2 \xrightarrow{H_2SO_4} [(C_2H_5)_2SiO]_x + 2CH_3COOC_2H_5 \qquad (VI)$$

The polydiethylsiloxanes obtained by reactions of monocarboxylic acids with diethyldiethoxysilane distilled practically completely at up to 200° (1 mm). Their fractional composition did not depend on the nature of the acid and its concentration, in contrast to the composition of the polydiethylsiloxanes formed by the reactions of mineral acids with diethyldiethoxysilane. This indicates that under the reaction conditions (temperature of not more than 125°), the monocarboxylic acids did not produce cleavage of the siloxane bond in the polymers formed, which in the case of mineral acids led to enlargement of the rings.

Investigation of the reactions of diethyldiethoxysilane with dicarboxylic acids (oxalic, succinic, adipic and maleic) led to the same rules as were established in the reaction with monocarboxylic acids. In the absence of catalysts, only the strongest, namely oxalic acid, led to the formation of polydiethylsiloxanes free from traces of linear polymers containing ethoxy groups in the molecule. Together with polydiethylsiloxanes, the reaction mixture contained neutral and acid esters of the dicarboxylic acids and free ethyl alcohol. The presence of a considerable amount of the latter and acid esters indicates that water formed in the process of the reaction by scheme (VII) produces hydrolysis of the neutral esters of the dicarboxylic acids formed.

$$(C_2H_5)_2Si(OC_2H_5)_2 + R(COOH)_2 \longrightarrow [(C_2H_5)_2SiO]_x + R(COOC_2H_5)_2 + H_2O \qquad (VII)$$

Thus, as a result of the reaction with maleic acid, besides its neutral ester of maleic acid, free fumaric acid and its acid ethyl ester were formed. It may be surmised that their formation occurs as a result of rearrangement and subsequent hydrolysis of the neutral ester of maleic acid, since rearrangement of free maleic acid or its acid ester during the reaction would be expected to give the neutral ester of fumaric acid, whose dissociation constant of the second carboxyl is two orders higher than that of maleic acid.

As in the reactions of diethyldiethoxysilane with monocarboxylic acids, traces of sulfuric acid in the reactions with dicarboxylic acids sharply accelerated the process and made it possible to reduce the excess acid required for the formation of polydiethylsiloxanes, free from traces of linear polymers with ethoxy groups.

The fractional composition of the polydiethylsiloxanes was similar to the composition obtained in reactions with monocarboxylic acids and also did not depend on the nature of the acid. Hence, we arrive at the conclusion that polydiethylsiloxanes are stable to the action of carboxylic acids.

EXPERIMENTAL

1. Action of monocarboxylic acids on diethyldiethoxysilane. A mixture of acid and diethyldiethoxysilane was heated to boiling in a flask with a reflux condenser. When the reaction mixture had been kept at the appropriate temperature for the required time, the ethyl ester of the particular acid was removed by distillation. The residue was cooled to room temperature and the layer of aqueous acid solution separated. The residue (polydiethylsiloxanes) was washed with water, a 1% solution of sodium carbonate (until neutral to phenolphthalein) and again with water until neutral. After being dried over calcium chloride, the residue was fractionated at 1 – 2 mm. In

experiments with monochloroacetic acid, the temperature was kept at 95 – 100° and the ethyl ester distilled off in vacuum. The yield of polydiethylsiloxanes varied over the range 90 – 96%. The yield of ethyl esters of the carboxylic acids was 80 – 90% after a second distillation. Table 2 shows data from some experiments characterizing the yield and composition of the polydiethylsiloxanes in relation to the reaction conditions.

2. Action of diethyldiacetoxysilane on diethyldiethoxysilane. 102 g of diethyldiacetoxysilane (b.p. 82 – 83° at 8 mm, acetyl number 57.82) and 88 g of diethyldiethoxysilane were heated to 88 – 90° in the presence of 0.5 g of ethylsulfuric acid for 3 hours in a flask with a reflux condenser. The ethyl acetate was then distilled off; after washing and a second distillation, the yield was 78 g (88.6%). The residue was washed with water to a neutral reaction, dried over calcium chloride and fractionated. The yield of polydiethylsiloxanes with b.p. 100 – 148° (1 mm) was 92 g (90%).

Found %: Si 27.48, 27.57; OC_2H_5 0.0. $C_4H_{10}OSi$. Calculated %: Si 27.45.

3. Action of dicarboxylic acids on diethyldiethoxysilane. a) 176 g of diethyldiethoxysilane and 99 g of anhydrous oxalic acid were heated with stirring for 4 hours at 100° in a flask with a reflux condenser. The ethyl alcohol (32 g) was then removed by distillation. The residue was cooled to room temperature and the upper layer (polydiethylsiloxane with a small amount of diethyloxalate) separated, washed with water until neutral, dried over calcium chloride and fractionated. We obtained polydiethylsiloxanes with b.p. 103 – 185° (1 mm) weighing 94 g (92%).

Found %: Si 27.40, 27.53; OC_2H_5 0.0. $C_4H_{10}OSi$. Calculated %: Si 27.45.

The lower layer of the reaction mixture was fractionated in vacuum. A second distillation of a fraction with b.p. 80° (12 mm) yielded 62 g of diethyl oxalate.

B.p. 183 – 184° (752 mm), n_D^{20} 1.4096, d_4^{20} 1.0790, MR 33.50. $C_6H_{10}O_4$. Calculated 33.45.

A second distillation of a fraction with b.p. 110 – 116° (12 mm) gave 54 g of the monoethyl ester of oxalic acid.

B.p. 114 – 115° (12 mm), n_D^{20} 1.4379, d_4^{20} 1.2176, MR 25.75. $C_4H_6O_4$. Calculated 25.66.

b) 176 g of diethyldiethoxysilane and 128 g of maleic acid (m.p. 129 – 130°) were heated for 8 hours with stirring in a flask with a reflux condenser. After removal of the alcohol, the reaction mixture was cooled to room temperature, when a precipitate formed. The weight of the dry precipitate was 7 g. After recrystallization from water it had m.p. 285 – 286° and an acid number of 965.0 (for fumaric acid: acid number 965.5, m.p. 286°). After separation from the fumaric acid, the rest of the reaction mixture was diluted with 100 ml of toluene; the separation of lustrous crystals began and these were separated after 12 hours, washed with toluene and dried. After recrystallization from toluene, the substance (yield 12 g) had m.p. 69.5°.

Acid number 388.41 – 389.07; hydrolysis number added to acid number 777.2 – 777.3 (for monoethyl ester of fumaric acid: m.p. 69°, acid number 388.88; acid number added to hydrolysis number 777.77).

After separation of the monoethyl ester of fumaric acid, the toluene solution of the reaction mixture was neutralized with a saturated solution of sodium bicarbonate; the toluene solution of diethyl maleate and polydiethylsiloxanes was separated, washed with water until neutral, dried over calcium chloride and fractionated. We obtained 37 g of diethyl maleate after a second distillation.

B.p. 95 – 96° (7 mm), n_D^{20} 1.4398, d_4^{20} 1.0683, MR 42.60. $C_8H_{12}O_4$. Calculated 42.24.

We obtained 100 g of polydiethylsiloxanes with b.p. 80 – 200° (1 mm).

Found %: Si 25.87, 25.61; OC_2H_5 5.2. $C_4H_{10}OSi$. Calculated %: Si 27.45; OC_2H_5 0.0.

4. Action of maleic, succinic and adipic acids on diethyldiethoxysilane in the presence of sulfuric acid. A mixture of diethyldiethoxysilane, dicarboxylic acid and sulfuric acid was heated at 100 – 105° with stirring in a flask with a reflux condenser. After an appropriate time, the alcohol was removed by distillation; the residue of the reaction mixture was diluted with benzene and neutralized with sodium bicarbonate. The benzene solution of polydiethylsiloxanes and neutral ethyl esters of the dicarboxylic acids was separated and washed with water until neutral; after drying over calcium chloride, the benzene was removed and the residue fractionated in vacuum. Table 3 gives the data of some experiments.

TABLE 2

Interaction of Diethyldiethoxysilane With Monocarboxylic Acids (In all the experiments, 1 mole of diethyldiethoxysilane was used)

Acids used in reaction (in moles)						Reaction time (in hours)	Temperature	Yield of polydiethylsiloxanes (in %)	Characteristics of polydiethylsiloxanes				
formic (concentration in %)	acetic (concentration) in %)	propionic, 99.6%	n-butyric, 99.7%	monochloroacetic, 100%	sulfuric (in g)				boiling point (1 mm)	yield (in %)		content (in %)	
										fraction	undistillable residue	Si	OC_2H_5
2(99.4)	–	–	–	–	–	3	63°	96	–	–	–	–	1.98
2(99.4)	–	–	–	–	–	6	63	97	–	–	–	–	1.84
2.2(99.4)	–	–	–	–	–	3	63	92	85-176°	93	7	27.32	0
2.4(99.4)	–	–	–	–	–	2	63	90	90-180	93	7	27 37	0
2.2(85)	–	–	–	–	–	10	66	97	–	–	–	–	2.43
2.5(85)	–	–	–	–	–	6	66	95	88-185	95	5	27.31	0
–	2.2(100)	–	–	–	–	6	87	88	–	–	–	–	1.16
–	2.2(100)	–	–	–	–	10	87	90	–	–	–	–	1.19
–	2.5(100)	–	–	–	–	6	87	92	91-200	96	4	27.26	0
–	2.5(80)	–	–	–	–	10	88	86	–	–	–	–	0.48
–	2.75(80)	–	–	–	–	12	88	88	–	–	–	–	0.11
–	2.2(80)	–	–	–	0.4	3	88	88	92-200	90	10.00	27.43	0
–	–	2.2	–	–	0.4	5	106	96	100-200	87.5	12.5	27.33	0
–	–	–	2.2	–	0.4	5	125	98	100-200	88	12	27.38	0
–	–	–	–	2	–	1	100	90	100-200	92	8	27.48	0

Footnote: The calculated silicon content of the cyclic polymer unit $(C_2H_5)_2SiO$ is 27.45%.

TABLE 3

Interaction of Diethyldiethoxysilane with Dicarboxylic Acids (In all experiments, 1 mole of diethyldiethoxysilane was used)

Acids used in reaction							Duration (in hrs)	Polydiethylsiloxanes •			Diethyl esters of dicarboxylic acids					
succinic		maleic		adipic		sulfuric (d 1.84) (in g)		yield (in %)	boiling point (1 mm)	Si content (in %)	yield (in %)	boiling pt. (pressure in mm)	nD^{20}	d^{20}_4	MR	
(in g)	(in mole)	(in g)	(in mole)	(in g)	(in mole)										fnd.	calc.
–	–	128	1.1	–	–	0.4	5	94	100-190°	27.26	42	95° (7)	1.4398	1.0683	42.60	42.24
130	1.1	–	–	–	–	0.4	5	90	103-195	27.19	71	216-218(752)	1.4198	1.0388	42.11	42.71
–	–	–	–	146••	1	0.4	5	67	103-160	27.43	17	108-109(11)	1.4280	1.0093	51.54	51.97
–	–	–	–	146	1	0.4	10	82	90-200	27.49	45	108-109(11)	1.4280	1.0093	51.54	51.97

• The OC_2H_5 group was absent.

•• Unreacted adipic acid (44 g) and diethyldiethoxysilane (58 g) were isolated.

SUMMARY

An investigation was made of the reactions of diethyldiethoxysilane with carboxylic acids. The dependence of the chemical composition of the polydiethylsiloxanes on the strength of the acid and its concentration and amount was determined. The effect of small amounts of sulfuric acid on the reaction rate and the chemical composition of the polydiethylsiloxanes was demonstrated.

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POLYDIETHYLSILOXANE LIQUIDS

IV. ACTION OF ALDEHYDES AND KETONES ON DIETHYLDIETHOXYSILANE

N. S. Leznov, L. A. Sabun and K. A. Andrianov

In previous communications [1 – 3] it was shown that the action of mineral and organic acids on diethyldiethoxysilane caused the formation of polydiethylsiloxanes and ethyl esters of the acids. Depending on the ratios of the starting components, the concentrations of the acids and the reaction conditions, the reactions of acids with diethyldiethoxysilane may give cyclic polydiethylsiloxanes or a mixture of them with linear polymers, containing ethoxyl groups at the ends of the chain.

Investigation showed that in the interaction of diethyldiethoxysilane with aqueous solutions of aldehydes the latter did not react and the process consisted of hydrolysis of the diethyldiethoxysilane by water by scheme (I).

$$(C_2H_5)_2Si(OC_2H_5)_2 + H_2O \xrightarrow{-C_2H_5OH} (C_2H_5)_2Si\begin{matrix}OH\\OH\end{matrix} + (C_2H_5)_2Si\begin{matrix}OC_2H_5\\OH\end{matrix} \xrightarrow{-H_2O}$$

$$\rightarrow [(C_2H_5)_2SiO]_x + (C_2H_5)_2Si(OC_2H_5)-O-\left[\begin{matrix}C_2H_5\\|\\Si-O\\|\\C_2H_5\end{matrix}\right]_{x'}-Si(C_2H_5)_2(OC_2H_5) \qquad (I)$$

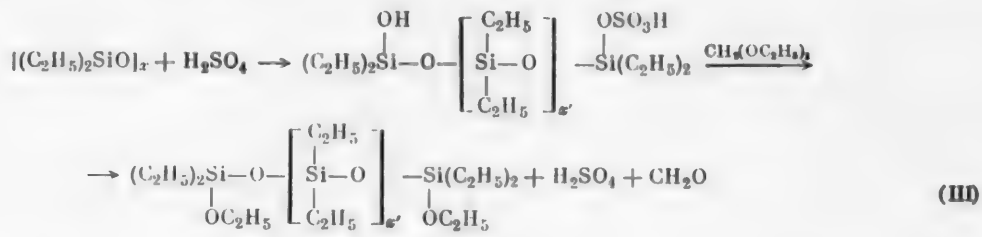
In the absence of catalysts, anhydrous aldehydes and acetone were inert as regards reactions with diethyldiethoxysilane; regardless of the time of heating of the reaction mixture, neither polydiethylsiloxanes nor acetals were detected in the reaction products. Mineral acids were tested as catalysts. Here it was found that hydrogen chloride and solutions of it did not produce interaction of the aldehydes with diethyldiethoxysilane, while 0.1 – 0.2% of sulfuric acid led to the formation of polydiethylsiloxanes and the corresponding acetals by scheme (II).

$$(C_2H_5)_2Si(OC_2H_5)_2 + RCHO \xrightarrow{H_2SO_4} RCH\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} + [(C_2H_5)_2SiO]_x +$$

$$+ (C_2H_5)_2Si(OC_2H_5)-O-\left[\begin{matrix}C_2H_5\\|\\Si-O\\|\\C_2H_5\end{matrix}\right]_{x'}-Si(C_2H_5)_2(OC_2H_5) \qquad (II)$$

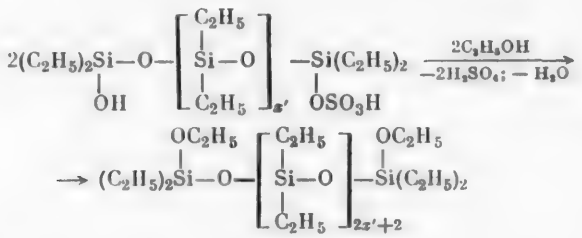
It was not possible to obtain polydiethylsiloxanes free from traces of polymers containing ethoxyl groups in the molecule by changing the reaction conditions or the quantitative ratios of diethyldiethoxysilane and aldehyde. Where acetaldehyde and butyraldehyde were used, the formation of polymers containing ethoxyl groups may be explained by hydrolysis of diethyldiethoxysilane with water (scheme I), formed as a result of crotonic condensation of the aldehyde. However, this explanation cannot be extended to the reaction with formaldehyde, for which a similar condensation is unknown.

It was previously established that in the interaction of diethyldiethoxysilane with carboxylic acids (with sufficient concentration and amounts of them), an increase in the heating time of the reaction mixture led to reduction or complete elimination of the formation of polymers containing ethoxyl groups in the molecule. A study of the reaction of diethyldiethoxysilane with formaldehyde (paraformaldehyde) showed that an increase in the heating time led to the formation of a mixture of polydiethylsiloxanes with an increased content of ethoxyl groups. This indicates the possibility of a reverse reaction between cyclic polydiethylsiloxanes and diethylformal in the presence of sulfuric acid by scheme (III).



(III)

Starting from scheme (III), it can also be proposed that the formation of polymers containing ethoxyl groups may also involve alcohol, liberated by hydrolysis of diethylformal by water, formed during the condensation of polydiethylsiloxane sulfates by scheme (IV).



(IV)

Schemes (III) and (IV) were demonstrated experimentally. The action of diethylformal and alcohol on cyclic polydiethylsiloxanes, treated with sulfuric acid, led to the formation of mixtures of polydiethylsiloxanes, which were found to contain 4 – 5% of ethoxy groups, respectively.

The reaction of acetone with diethyldiethoxysilane in the presence of traces of sulfuric acid proceeded with the formation of a mixture of polydiethylsiloxanes, however, ketals were not detected in the reaction products. Together with polydiethylsiloxanes, the reaction product contained alcohol and a considerable amount of soluble resins, formed as a result of condensation of both acetone and, apparently, ketal. Since the resins were soluble in the same solvents as the polydiethylsiloxanes, they could not be separated. Distillation of the mixture in vacuum was accompanied by decomposition.

EXPERIMENTAL

1. Action of formaldehyde on diethyldiethoxysilane. A mixture of diethyldiethoxysilane and dry paraformaldehyde was heated in the presence of 0.2% of sulfuric acid (d 1.84) in a flask with a reflux condenser. After an appropriate time, the diethylformal was distilled from the reaction mixture and distilled a second time. The residue was washed with water until neutral, dried over calcium chloride and fractionated at 1 – 2 mm. The data from some experiments are presented in Table 1.

2. Action of acetaldehyde and n-butyraldehyde on diethyldiethoxysilane. The experiments were performed under the conditions given in Exp. 1. On reaching 40°, the reaction mixture acquired a brown color; as it was heated, it deposited a precipitate, which was separated by filtration after evaporation of the acetal. In the reaction with butyraldehyde, a resin remained in the solution of polydiethylsiloxanes. The data of some experiments are given in Table 2.

TABLE 1

Interaction of Diethyldiethoxysiloxane with Paraformaldehyde (In all experiments 0.5 mole of diethyldiethoxysilane and 0.66 mole of paraformaldehyde were used in the reaction. The temperature was 90°)

Duration of experiment (in hours)	Yield (in %)		Characteristics of polydiethylsiloxanes		
	polydiethyl-siloxanes	diethyl-formal	boiling point (1 mm)	content (in %)	
				Si	OC_2H_5
1	86	75.5	95-180°	24.98	7.85
3	92	71.5	105-200	26.72	2.4
8	90	60	90-200	25.81	5.45
10	85	57	88-200	25.49	6.15

Footnote. The calculated Si conten of a cyclic polymer unit is 27.45%. The OC_2H_5 groups were determined by the Zeisel method.

TABLE 2

Interaction of Diethyldiethoxysilane with Paraldehyde and n-Butyraldehyde (In all experiments 0.5 mole of diethyldiethoxysilane was used in the reaction. The temperature was 90°)

Expt. No.	Used for reaction (mole)		Duration of experiment (in hours)	Yield (in %)		Characteristics of polydiethylsiloxanes		
	paraldehyde	n-butyraldehyde		polydiethyl-siloxanes	diethyl-formal	boiling point (1 mm)	content (in %)	
							Si	OC_2H_5
1	0.5	–	4	84	76	90-149°	25.70	5.85
2	0.66	–	6	81	64	113-165	26.49	1.87
3	0.66	–	10	83	57	101-167	26.58	1.96
4	–	0.5	1	97	58	95-246	24.69	7.49
5	–	0.66	4	92	58	100-250	23.80	10.04

Footnote. See footnote in Tables 1 – 2. The yield of resin, not containing silicon, was 3 – 5 g in experiments 1 – 3.

3. Action of acetone on diethyldiethoxysilane. An equimolecular mixture of diethyldiethoxysilane and anhydrous acetone containing 0.2% of sulfuric acid (d 1.84) or 0.3% of toluenesulfonic acid was heated for 1 – 8 hours to 40 – 80° on a water bath in a flask with a reflux condenser. The alcohol was distilled from the reaction mixture. The residue was washed with water until neutral, dried over calcium chloride and fractionated at 1 mm. Diethyl ketal was not detected in the alcohol distilled off or in the products from fractionation of the rest of the reaction mixture. When the vapor temperature reached 130 – 140°, distillation of the polydiethylsiloxanes was accompanied by strong decomposition and the condensate had a brown color. The ethoxy group content of the fractions obtained was from 3.5 to 12.4%.

4. Action of diethylformal on cyclic polydiethylsiloxanes. 51 g of cyclic polydiethylsiloxanes (27.43% silicon content) with b.p. 180 – 200° (1 mm), free from polymers containing ethoxy groups, and 0.4 g of sulfuric acid (d 1.84) were stirred together for 5 minutes at 30 – 40°; 35 g of diethylformal was then added and the mixture heated at 90 – 95° for 5 hours. After this, the diethylformal was removed by distillation and the residue cooled to room temperature, washed with water until neutral, dried over calcium chloride and fractionated.

We obtained 49 g of polydiethylsiloxanes boiling above 180° at 1 mm.

Found %: OC_2H_5 5.17, 5.29. $C_4H_{10}OSi$. Calculated %: OC_2H_5 0.0.

5. Action of alcohol on cyclic polydiethylsiloxanes. 51 g of cyclic polydiethylsiloxanes and 5 g of sulfuric acid (96 – 100%) were stirred together for 10 minutes at room temperature and then the mixture was poured into 30 ml of anhydrous alcohol and shaken for 3 – 5 minutes. After 30 minutes, the ethylsulfuric acid layer was separated and the residue washed with water until neutral, dried over calcium chloride and fractionated. We obtained 50 g of polydiethylsiloxanes boiling above 180° at 1 mm.

Found %: OC_2H_5 3.63, 3.76. $C_4H_{10}OSi$. Calculated %: OC_2H_5 0.0.

SUMMARY

1. The interaction of anhydrous aldehydes with diethyldiethoxysilane in the presence of traces of sulfuric acid led to the formation of diethylacetals and cyclic polydiethylsiloxanes, containing traces of linear polymers with ethoxyl groups at the ends of the chain.

2. Cyclic polydiethylsiloxanes could be rearranged into linear polymers with ethoxy groups at the ends of the chains by the action of diethylformal or alcohol in the presence of traces of sulfuric acid.

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* Original Russian pagination. See C. B. Translation.

POLYDIETHYLSILOXANE LIQUIDS

V. A CONTRIBUTION ON THE MECHANISM OF THE REACTION OF DIETHYLDIETHOXYSILANE WITH ACETIC ACID

N. S. Lesnov, L. A. Sabun and K. A. Andrianov

Previously* it was established that heating diethyldiethoxysilane with monocarboxylic acids led to the formation of polydiethylsiloxanes and ethyl esters of the corresponding acids according to scheme (I).

$$(C_2H_5)_2Si(OC_2H_5)_2 + 2RCOOH \longrightarrow$$

$$\longrightarrow \underset{(a)}{[(C_2H_5)_2SiO]_x} \qquad {}_2Si(OC_2H_5)-O-\left[\begin{matrix}C_2H_5\\ |\\ Si-O\\ |\\ C_2H_5\end{matrix}\right]_{x'}-Si(OC_2H_5)_2 + 2RCOOC_2H_5 + H_2O \quad (I)$$

(b)

Depending on the reagent ratios, concentration of acids and catalysts, it was possible to obtain cyclic polymers (a) or mixture of them with linear polymers (b).

On investigating the reaction of diethyldiethoxysilane with acetic acid it was also established that removal of the ethyl acetate formed in the reaction by scheme (I) from the reaction mixture sharply reduced the reaction rate and the composition of the polydiethylsiloxanes was enriched in linear polymers with ethoxy groups at the ends of the molecule chains. This observation indicates that the formation of ethyl acetate is not the first stage in the process, as would be expected according to scheme (II).

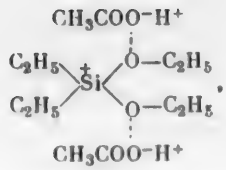
$$(C_2H_5)_2Si(OC_2H_5)_2 + 2CH_3COOH \longrightarrow (C_2H_5)_2Si\begin{matrix}OH\\ OH\end{matrix} + 2CH_3COOC_2H_5 \quad (II)$$

To establish the nature of the initial stage of the reaction between diethyldiethoxysilane and acetic acid, experiments were carried out in a toluene medium with continuous distillation of the volatile reaction products. It was then found that polydiethylsiloxanes and ethyl acetate were not formed. Diethyldiacetoxysilane and unchanged diethyldiethoxysilane were found in the reaction products. Free alcohol was found in the condensate. These data make it possible to represent the initial stage of the reaction of diethyldiethoxysilane with acetic acid by scheme (III).

$$(C_2H_5)_2Si(OC_2H_5)_2 + 2CH_3COOH \longrightarrow (C_2H_5)_2Si\begin{matrix}OCOCH_3\\ OCOCH_3\end{matrix} + 2C_2H_5OH \quad (III)$$

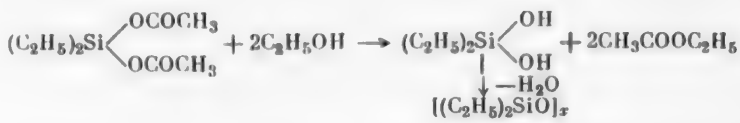
Scheme (III) is in agreement with accepted ideas on reactions proceeding through onium compounds. On considering the compound

* See Communication III, J. Gen. Chem., 29, 1508 (1959).



it can be seen that the silicon atom carrying the positive charge attracts the electronegative acetoxy group to the greatest extent and due to this decomposition of the complex, proceeds with the elimination of alcohol and the formation of diethyldiacetoxysilane.

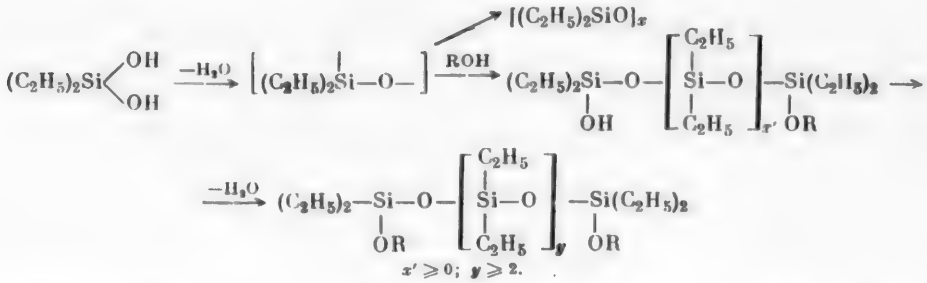
Scheme (III) provides a basis for considering that the formation of ethyl acetate and diethyldihydroxysilane, which is converted into polydiethylsiloxanes with the loss of water, begins with the action of alcohol on diethyldiacetoxysilane by scheme (IV).



(IV)

To confirm the possibility of the formation of polydiethylsiloxanes by scheme (IV) an investigation was made of the reaction of anhydrous alcohol with diethyldiacetoxysilane. It was established that heating methyl, ethyl and n-butyl alcohols with diethyldiacetoxysilane led to the formation of the corresponding esters of acetic acid and a mixture of polydiethylsiloxanes. In the presence of traces of sulfuric acid, the formation of the latter began at room temperature.

Investigation of the chemical composition of the polydiethylsiloxanes obtained according to scheme (IV) showed that together with cyclic polymers, they contained linear polymers with alkoxyl groups at the terminal silicon atoms. Such polymers may be formed as a result of the elimination of alcohol from the polymer chain, produced by dehydration of diethyldihydroxysilane by scheme (V).



(V)

Scheme (V) was confirmed experimentally by experiments on the dehydration of diethyldihydroxysilane. Data from these experiments showed that heating diethyldihydroxysilane in a xylene medium led to practically complete evolution of water with the formation of polydiethylsiloxanes, whose chemical analysis and physical constants indicated their cyclic structure.

Heating diethyldihydroxysilane in an anhydrous alcohol medium led to a mixture of polymers in which there were linear polymers containing ethoxyl groups. The amount of the latter was affected by the acidity of the medium. Thus, dehydration of diethyldihydroxysilane in an alcohol medium, containing traces of sulfuric and acetic acids, gave polydiethylsiloxanes containing 3.58 and 5.47% of ethoxyl groups, respectively; in the absence of acid, the ethoxyl group content did not exceed 2%.

Scheme (III) gives a basis also for proposing the possibility of the formation of polydiethylsiloxanes as a result of polycondensation of diethyldiacetoxysilane with diethyldiethoxysilane with the liberation of ethyl acetate by scheme (VI).

$$(C_2H_5)_2Si\begin{matrix}OCOCH_3\\OCOCH_3\end{matrix} + \begin{matrix}C_2H_5O\\C_2H_5O\end{matrix}Si(C_2H_5)_2 \longrightarrow [(C_2H_5)_2SiO]_x + 2CH_3COOC_2H_5 \qquad (VI)$$

It was established experimentally that the reaction of scheme (VI) occurred in the presence of traces of sulfuric or ethylsulfuric acid.

EXPERIMENTAL

1. Action of acetic acid on diethyldiethoxysilane. 44 g of diethyldiethoxysilane, 30 g of glacial acetic and 100 ml of dry toluene were heated at 90 – 95° for 12 hours in a Favorskii flask, connected to a distillation condenser. Then the toluene, acetic acid and part of the unreacted diethyldiethoxysilane were distilled from the reaction mixture until the temperature of the vapor was 155°. The residue was fractionated at 16 mm. Fractions boiling above 70° were analyzed for diethyldiacetoxysilane content by titration with 1 N sodium hydroxide solution. The analysis data are presented in Table 1. A second distillation of the condensate, distilled from the reaction mixture, yielded a fraction with b.p. 70–79°, which was neutralized with dry sodium carbonate, dried over sodium sulfate and treated with α-naphthyl isocyanate. The α-naphthylurethan precipitated was washed with petroleum ether. After drying, the product had m.p. 84.5°.

TABLE 1

Diacetoxydiethylsilane Content of Reaction Products of Diethyldiethoxysilane with Acetic Acid

Fractions		1 N NaOH sol.	Diethyldiacetoxy-
boiling pt. (16 mm)	weight (g)	used in titr. (ml)	silane content (in %)
70-80°	12	0.6	0.51
80-81	5	3.7	7.55
81-83	4.5	4.8	10.96
83-87	5.2	13.5	26.52
87-94	3.1	9.4	30.94
94-95	3.6	22	62.40
95	2	16	81.60

Footnote: When shaken with a 20% aqueous solution of sodium sulphite, the still residue (2 g) was converted into diethyldihydroxysilane; after recrystallization from toluene, the substance had m.p. 96°.

2. Diethyldiacetoxysilane. This material was obtained by heating 1 mole of diethyldiethoxysilane and 2.05 moles of acetic anhydride in the presence of traces of sulfuric acid with the simultaneous removal of the ethyl acetate by distillation and subsequent fractionation of the reaction mixture. The yield of diethyldiacetoxysilane with b.p. 82 – 83° (8 mm) was 178 g (87%).

Found %: CH_3COO 57.58, 57.39. $C_8H_{16}O_4$. Calculated %: CH_3COO 57.84.

3. Action of alcohols on diethyldiacetoxysilane. A mixture of diethyldiacetoxysilane and anhydrous alcohol was boiled in a flask with a reflux condenser. After an appropriate period of heating, the corresponding ester of acetic acid was removed by distillation. The rest of the reaction mixture was washed with water, a 1% solution of sodium carbonate (phenolphthalein) and again with water until neutral, dried over calcium chloride and vacuum distilled. Data from the experiments and the characteristics of the polydiethylsiloxanes formed are presented in Table 2.

TABLE 2

Interaction of Alcohols With Diethyldiacetoxysilane (In all experiments, 41 g of diethyldiacetoxysilane was used for the reaction)

Alcohol used in reaction (in g)			Temp. °C	Duration (in hours)	Products obtained (in g)		Characteristics of polydiethylsiloxanes		
								content (in %)	
methyl	ethyl	n-butyl			ester of acetic acid	polydiethyl-siloxanes	boiling pt. (3 mm)	Si	OC_2H_5
14	–	–	66°	2	25	19.7	103-165°	26.39	3.71
–	20	–	88	6	27	24	103-182	25.91	6.88
–	–	30	120	9	27.6	28	103-196	24.59	10.5

4. Diethyldihydroxysilane. 51 g of diethyldiacetoxysilane was added in one portion to a mixture of 200 g of a 20% aqueous solution of sodium sulfite and 70 g of finely powdered ice. After 3 – 5 minutes of vigorous shaking, the crystalline precipitate of diethyldihydroxysilane was collected by filtration, washed with a 5% solution of sodium sulfite cooled to 0°, pressed out between sheets of filter paper and recrystallized from a mixture of benzene and diethyl ether. The yield of the recrystallized product was 27 – 28 g (90 – 93%). The m.p. was 96 – 97°.

Found %: C 40.20, 40.17; H 10.09, 10.04; Si 22.58, 23.41. $C_4H_{12}O_2Si$. Calculated %: C 40.00; H 10.06; Si 23.34.

5. Dehydration of diethyldihydroxysilane. a) In a xylene medium. 30 g of diethyldihydroxysilane and 50 ml of dry xylene were boiled for 8 hours in a flask, connected to a reflux condenser through a water trap. 4.3 ml of water was collected in the trap. After evaporation of the the xylene from the reaction mixture by heating at 150° (50 mm), the residue was fractionated. We obtained polydiethylsiloxanes with b.p. 100 – 150° (1 mm) weighing 24 g (94.9%).

Found %: Si 27.48, 27.35. $C_4H_{10}OSi$. Calculated %: Si 27.45.

b) In an alcohol medium. 1) 30 g of diethyldihydroxysilane and 100 ml of anhydrous alcohol were boiled for 10 hours in a flask with a reflux condenser and then the alcohol was removed by distillation. The residue was diluted with 50 ml of toluene, washed with water, dried over calcium chloride and fractionated after removal of the toluene. We obtained 23 g of polydiethylsiloxanes with b.p. 101 – 146° (1 mm).

Found %: OC_2H_5 1.61, 1.51.

2) The experiment was repeated, but with the alcohol containing 0.3 g of sulfuric acid (d 1.84). We obtained 24 g of polydiethylsiloxanes with b.p. 104 – 150° (1 mm).

Found %: OC_2H_5 3.50, 3.72.

3) The experiment was repeated, but with the alcohol containing 0.3 g of glacial acetic acid. We obtained 25 g of polydiethylsiloxanes with b.p. 104 – 150° (1 mm).

Found %: OC_2H_5 5.34, 5.60. $C_4H_{10}OSi$. Calculated %: OC_2H_5 0.0.

6. Action of diethyldiactoxysilane on diethyldiethoxysilane. 102 g of diethyldiacetoxysilane and 88 g of diethyldiethoxysilane was heated for 4 hours at 88 – 90° in the presence of 0.5 g of ethylsulfuric acid in a flask with a reflux condenser; the ethyl acetate (78 g, i.e. 88%, after washing and a second distillation) was removed by distillation. The residue was washed with water until neutral, dried over calcium chloride and fractionated. We obtained 92 g (90%) of polydiethylsiloxanes. The b.p. was 98 – 148° (1 mm).

Found %: Si 27.48, 27.57; OC_2H_5 0.0. $C_4H_{10}OSi$. Calculated %: Si 27.45.

SUMMARY

1. In the interaction of acetic acid with diethyldiethoxysilane, diethyldiacetoxysilane is formed in the first stage.

2. The interaction of alcohols with diethyldiacetoxysilane leads to the formation of polydiethlsiloxanes and the corresponding esters of acetic acid.

3. Dehydration of diethyldihydroxysilane in an alcohol medium gives a mixture of cyclic polydiethylsiloxanes with linear polymers containing ethoxyl groups at the ends of the molecule chains.

4. The interaction of diethyldiethoxysilane with diethyldiacetoxysilane in the presence of ethylsulfuric or sulfuric acid leads to the formation of cyclic polydiethylsiloxanes and ethyl acetate.

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CATALYTIC OXIDATION OF PROPYLENE TO ACROLEIN. I

O. V. Isaev, L. Ya. Margolis and S. Z. Roginskii

Institute of Physical Chemistry, Academy of Sciences, USSR

The process of catalytic oxidation of propylene to acrolein has been studied very little [1], although the direct oxidation of propylene with oxygen is the most promising method for the preparation of this valuable product.

In 1945 patents appeared abroad on the oxidation of propylene on a copper catalyst [2]. According to the patent data, cupric or cuprous oxide was deposited on a carrier. For industrial testing, a catalyst was proposed consisting of copper oxides deposited on carborundum. Recently N. I. Popov et al. [3] published data on the catalytic activity of cuprous oxide deposited on silica gel and carborundum.

The purpose of the present work was a study of the properties of a cuprous oxide catalyst, used for the catalytic oxidation of propylene into acrolein, and a comparison of its activity with that of other oxidizing catalysts.

EXPERIMENTAL

All experiments were carried out in a dynamic apparatus at atmospheric pressure. A mixture of gases, consisting of propylene (15%), oxygen (15%) and nitrogen, was introduced into a quartz reactor filled with the catalyst investigated. The contact time was 2 seconds. The propylene was obtained in the same apparatus by dehydration of isopropyl alcohol over aluminum oxide and freed from ether, aldehydes, unreacted alcohol and traces of CO_2. The temperature in the reactor was maintained with an accuracy of ± 0.5° by means of a thermoregulator, based on a PP potentiometer. The thermoregulator was controlled with a Nichrome-Constantan thermocouple, placed in the center of the catalyst bed. The fall in temperature in a bed 2.5 – 3.0 cm long in the reactor was 5 – 7° during the oxidation of propylene. On the basis of results obtained previously [4] from a study of the phase composition of copper oxide catalysts for the oxidation of propylene into acrolein, the catalysts were prepared by impregnating pumice or carborundum with a definite volume of an aqueous solution of $Cu(NO_3)_2$ with subsequent drying and firing at 500 – 550° for 2 – 3 hours. X-ray analysis showed complete decomposition of the copper nitrate to CuO. Other catalysts on pumice were prepared by impregnating the carrier with the appropriate ammonium salt of the metal with subsequent firing in a crucible furnace at 500 – 550° for 2 – 3 hours.

The gases at the reactor inlet were analyzed periodically. During an experiment, 2 – 3 samples were taken at the outlet and the CO_2, C_3H_6, O_2 and CO in them determined by means of a VTI gas analyzer. At the end of the experiment, in each sample we determined the total aldehydes by the hydroxylamine method and the acrolein by bromination of the double bonds (bromide-bromate method).

DISCUSSION OF RESULTS

1. Oxidation of propylene over a copper catalyst. There is hardly any work in the literature on the mechanism of the oxidation of propylene into acrolein. It is impossible to set up a highly selective process without solving the problem of the origin of the carbon dioxide formed. In particular it is not clear whether the CO_2 is formed from the acrolein or if not from the aldehyde, through unstable intermediate products.

To elucidate the role of acetaldehyde in the oxidation of propylene, tracer methods were used. Oxidation of a mixture of propylene with oxygen and with acetaldehyde labeled with radioactive carbon (1 : 2 : 0.5) over

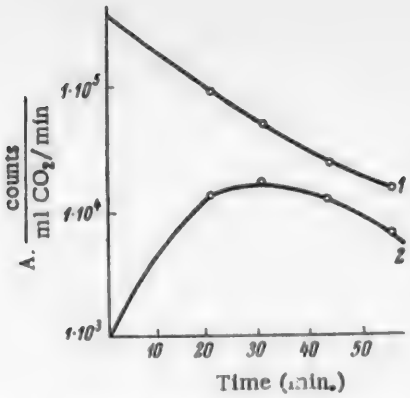

Fig. 1. Change in the specific radioactivities of acetaldehyde (1) and carbon dioxide (2) during the oxidation with oxygen of a mixture of propylene and acetaldehyde, labeled with C^{14}, over Cu_2O at 350°.

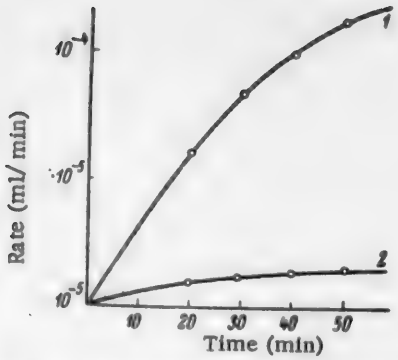

Fig. 2. Rate of formation of carbon dioxide (1) and consumption of acetaldehyde (2) during the oxidation of propylene over Cu_2O at 350°.

cuprous oxide at 350° made it possible to define the genetic link between these reaction products. The results of a typical experiment are presented in Fig. 1. The decrease in the specific activity of the acetaldehyde shows that during the oxidation reaction, unlabeled acetaldehyde is formed from the propylene and that this dilutes the radioactive acetaldehyde introduced into the system. The curve of the change in specific activity of the carbon dioxide passes through a maximum and does not intersect the specific activity curve of the acetaldehyde. Consequently, carbon dioxide is mainly formed not from acetaldehyde, but by an independent method through other intermediate products.

The results of processing the data by the kinetics method of M. B. Neiman [5] are presented in Fig. 2. Comparison of the rates of total carbon dioxide formation and of acetaldehyde conversion supports the conclusion that the bulk of the CO_2 in the oxidation of propylene is formed independently of the acetaldehyde.

These results agree with the conclusions we arrived at previously [6] on the oxidation of ethylene into ethylene oxide on silver and of propylene into aldehydes on V_2O_5. By the use of radioactive carbon, it was established that in these processes several parallel reactions proceeded simultaneously and independently with the formation of unstable intermediate products of the peroxide type. Under the conditions of the process, for acrolein the conversion into carbon dioxide seems more probable. In addition, the presence of the carrier in the reaction zone may facilitate decomposition of the acrolein.

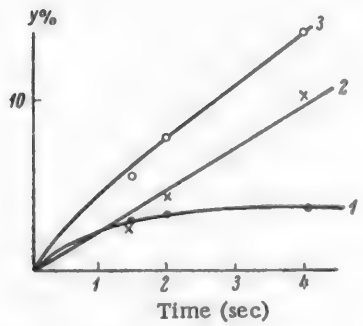

Fig. 3. Dependence of the degree of conversion of propylene (Y) on contact time at 400° (0.25% Cu on pumice). 1) C_3H_4O, 2) CO_2, 3) total degree of conversion.

To obtain a qualitative answer to the problems presented, some experiments were carried out to examine the effect of contact time on the oxidation of propylene and the results of these are presented in Fig. 3. With an increase in contact time, the acrolein yield at first increased and then became constant, with a continuous increase in the carbon dioxide yield. It might be expected that with an increase in contact time, the rate of formation and decomposition of acrolein would become commensurate. A preliminary rough calculation shows the similarity of the activation energies of acrolein and carbon dioxide formation.

To demonstrate the possible decomposition of acrolein, a mixture of acrolein, oxygen and nitrogen was passed over a catalyst (10% Cu on pumice) at 400°. The acrolein content of the mixtures was varied from 0.5 to 5%. The oxygen concentration of the original mixture was always 15%. With mixtures of these compositions, the acrolein was converted into carbon dioxide and the oxygen from the gas reaction mixture was completely consumed over the catalyst. Decreasing the concentration of copper on the carrier to 0.25% lowered the rate of extensive acrolein oxidation by a factor of several times. A copper content of 1.0% on carborundum promoted combustion of acrolein.

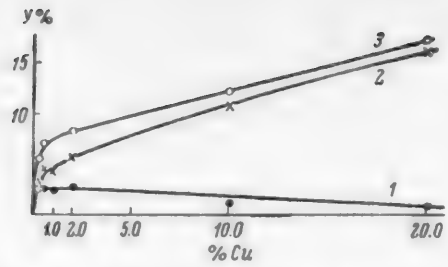

Fig. 4. Dependence of degree of propylene conversion (Y) on concentration of copper on pumice at 350°. 1) C_3H_4O, 2) CO_2, 3) total degree of conversion.

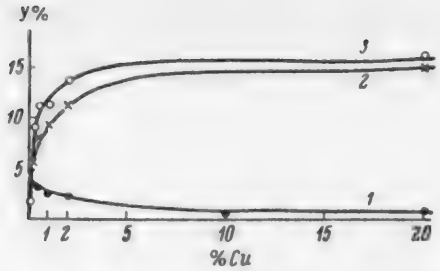

Fig. 5. Dependence of degree of propylene conversion on concentration of copper on pumice at 400°. 1) C_3H_4O, 2) CO_2, 3) total degree of conversion.

During the oxidation of propylene on a copper catalyst, the acrolein was not completely decomposed. There are probably two simultaneous and independent reactions, namely, the formation of acrolein and its oxidation to carbon dioxide. The concentration of oxygen in the reaction mixture was insufficient for both reactions and the ratio of the rates of these processes was determined by the composition of the gas mixture. On the basis of these qualitative data, the scheme for the oxidation of propylene into acrolein on a copper catalyst may be represented in the following way:

$$CH_3CH{=}CH_2 + O_2 \begin{cases} \nearrow CH_2{=}CH{-}CHO \longrightarrow CO_2 + H_2O \\ \searrow CO_2 + H_2O \end{cases}$$

Further work on determining the successive and parallel reactions in this process with the use of radioactive carbon will make it possible to refine this scheme.

If the oxidation of acrolein proceeds on copper oxide, then the acrolein yield should depend on the concentration of catalyst on the carrier. Several samples of catalyst deposited on pumice and carborundum were tested (see Figs. 4 – 7). The acrolein yield increased with a decrease in Cu_2O concentration on the carrier and passed through a maximum at 0.25% Cu on pumice and 0.1% Cu on carborundum, while the CO_2 yield and the total degree of conversion of propylene fell. The selectivity of the oxidation of propylene into acrolein increases sharply with a decrease in the concentration of Cu_2O on the carrier, which also indicates that the formation and decomposition of acrolein are successive reactions. The character of the curves obtained on a porous carrier, pumice, and one of low porosity, carborundum, are identical, indicating that the porosity of the carrier has an insignificant effect on the oxidation of propylene into acrolein.

Electron diffraction examination of the copper catalysts showed that when acrolein was passed over their surface, polymers were formed. It is probable that the formation of polymers is the reason for poisoning of the catalyst on prolonged operation. In connection with this, regeneration of the catalyst must consist of two operations: 1) treatment of the catalyst with oxygen to burn off the polymers from the surface, 2) reduction of the cupric oxide (formed during the first operation) to cuprous oxide with propylene or the reaction mixture. It is probable that the introduction of a series of additives to the cuprous oxide catalyst could considerably reduce the rate of acrolein polymerization and hence prolong the work life of the catalyst.

The selectivity of the process may be increased by reducing the contact time, by increasing the linear flow rate and also by decreasing the concentration of copper on the catalyst, to guarantee that the process proceeds in the kinetic region. Under certain process conditions, the length of the catalyst bed may be of great importance.

Another method of changing the selectivity of the process could be the introduction of various additives into the catalyst and this is the subject of the next communication.

2. Oxidation of propylene on other catalysts. It was previously [1] shown that oxides of metals of the 5th and 6th groups of the periodic system, namely, V_2O_5, MoO_3, WO_3 and UO_3, promoted the oxidation of unsaturated

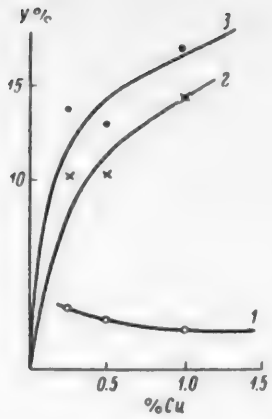

Fig. 6. Dependence of degree of propylene conversion on concentration of copper on pumice at 450°. 1) C_3H_4O, 2) CO_2, 3) total degree of conversion.

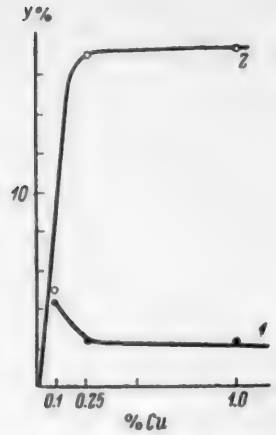

Fig. 7. Dependence of degree of propylene conversion on concentration of copper on carborundum at 400°. 1) C_3H_4O, 2) CO_2.

hydrocarbons with rupture of the double bond and, in the case of propylene, the formation of formaldehyde and acetaldehyde. However, these investigations were carried out with high concentrations of catalyst on the carrier and under these conditions, decomposition of acrolein is possible. In this connection, an investigation was again made of catalysts containing V_2O_5, WO_3 and MoO_3. Passing a mixture of propylene, nitrogen and oxygen over Cr_2O_3, MoO_3 and WO_3, deposited on pumice, showed that a considerable amount of acrolein was formed over these catalysts, but parallel with this process there was destructive oxidation of propylene with rupture of the doub'e bond and considerable formation of saturated aldehydes. The activity of the catalysts listed fell in going from Cr_2O_3 to WO_3.

Oxidation of propylene over V_2O_5 deposited on pumice showed that a noticeable amount of acrolein was formed at 400°. Raising the temperature led to an increase in the acrolein yield. The most active catalysts for the oxidation of propylene into aldehydes were found to be MoO_3 and V_2O_5, but they were not selective as regards the formation of acrolein. It was previously shown that acrolein was decomposed over CuO and that by decreasing the catalyst concentration on the carrier, it was possible to raise both the acrolein yield and the selectivity of the process. It seemed quite interesting to investigate the analogous relation for MoO_3 and V_2O_5, deposited on pumice. It was found that the acrolein yield on these catalysts depended little on the concentration of metal oxide on the pumice (up to 20% oxide).

The yield of saturated aldehydes (acetaldehyde and formaldehyde) on MoO_3 increased with a decrease in the concentration of metal oxide on the carrier. With an increase in temperature, the rate of propylene oxidation into saturated aldehydes became less than the rate of acrolein formation. It is probable that the activation energy of the oxidation of propylene into acrolein is considerably greater than the activation energies of the reactions whereby saturated aldehydes are formed. It is interesting to note there is practically no complete oxidation of propylene on MoO_3 deposited on pumice. The CO_2 yield was about 1%, even at 550°. Over V_2O_5, the yield of saturated aldehydes increased with an increase in the concentration of catalyst on the carrier. Simultaneously with this, the yield of CO and CO_2 increased.

An attempt to obtain the intermediate products in the oxidation of propylene over metallic silver in the range 200 – 400° did not lead to the desired results. Only traces of aldehydes and large amounts of CO_2 were found.

Besides these generally recognized catalysts of mild oxidation, an investigation was made of the activity of mixed catalysts (metal oxides, CuO + MoO_3 and CuO + V_2O_5) and the spinel, $CuAl_2O_4$. At 450–500° over these catalysts, propylene was oxidized into saturated aldehydes, acrolein and CO_2. In comparison with the cuprous oxide catalyst, the mixed catalysts produced an increase in the yield of saturated aldehydes and a sharp fall in the CO_2 yield. The conversion of propylene into acrolein was considerably less than on Cu_2O.

An investigation of semiconductor catalysts of the CdTe, CuSe, CuTe and Cu_3As type showed that on these catalysts the yield of carbon dioxide fell sharply, although the yield of acrolein was also low. The formation of noticeable amounts of saturated aldehydes was observed on CdTe, while they were hardly formed at all on CuSe, CuTe and Cu_3As. Decomposition of the catalyst under the process conditions was observed in the oxidation of propylene on copper selenide.

Thus, of the catalysts we examined, copper selenide, telluride, and arsenide, and cuprous oxide are the most selective as regards the formation of acrolein. Oxides of transition metals (MoO_3, V_2O_5 etc.) are active catalysts as regards the formation of mixtures of saturated aldehydes and acrolein.

SUMMARY

1. By a tracer method it was established that acetaldehyde is not the main intermediate for carbon dioxide formation in the oxidation of propylene.

2. It was found that acrolein is oxidized over a copper catalyst. The degree of oxidation of the acrolein depends on the concentration of catalyst on the carrier.

3. A hypothesis was put forward on a successive-parallel mechanism for the oxidation of propylene to acrolein.

4. An investigation was made of the effect of catalyst concentration on the carrier on the oxidation of propylene into acrolein.

5. A study was made of a series of catalysts (V_2O_5, MoO_3, WO_3, Cr_2O_3, CdTe, CuSe, CuTe, Cu_3As) for the oxidation of propylene into acrolein and the possibility of using catalysts not containing copper oxides was demonstrated.

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INVESTIGATION IN THE FIELD OF ALKOXYSILANES

XIV. CLEAVAGE OF ORGANOSILOXANES BY ALCOHOLS AS A METHOD OF SYNTHESIZING ORGANOALKOXYSILANES •

M. G. Vornokov and Z. I. Shabarova

Institute of Silicate Chemistry, Academy of Sciences, USSR

It has been known for a long time [3 – 9] that organosiloxanes are decomposed by hydroxides of alkali metals with the formation of the corresponding silanolates and silanols (eq. 1). On the other hand, there are reports in the literature [10 – 12] on the possibility of the reaction of silanols with alcohols leading to the formation of alkoxysilanes (eq. 2).

It seemed interesting to us to combine the two reactions given above to produce a method of synthesizing organoalkoxysilanes by cleaving organosiloxanes with alcohols in the presence of alkalis by the scheme: ••

$$\equiv SiOSi\equiv + MOH \rightleftarrows \equiv SiOM + HOSi\equiv \quad (1)$$

$$\equiv SiOH + HOR \rightleftarrows \equiv SiOR + HOH \quad (2)$$

$$\equiv SiOM + HOH \rightleftarrows \equiv SiOH + MOH, \text{ etc.} \quad (3)$$

which may be represented in a general form by equation (4), where M is an atom of an alkali metal

$$\equiv SiOSi\equiv + 2ROH \overset{MOH}{\rightleftarrows} 2\equiv SiOR + H_2O \quad (4)$$

However, since reaction (4) is reversible, for it to have a preparative character, it is necessary to remove the water formed from the reaction sphere.

Experimental data confirmed the hypothesis presented. We established that when linear, branched or cyclic organosiloxanes were heated with primary or secondary alcohols, boiling above 100° (one of the reagents was taken in excess), in the presence of 1 – 10 mole % of a hydroxide or an alcoholate of an alkali metal (preferably KOH), ••• accompanied by continuous azeotropic distillation of the water formed (boiling with a reflux condenser fitted with a water trap), the corresponding organoalkoxysilanes were formed in a yield of up to 70%. •••• The reaction

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• For previous communication see [1]. For preliminary communication see [2].

•• There is some information in the literature [12, 13] on the possibility of achieving such a reaction, but it is not of preparative interest [12, 13]. Patent data [14] which recently appeared on the problem examined in the article only became known to us after the publication of the preliminary communication [2].

••• Under the reaction conditions, hydroxides of alkali metals were converted into alcoholates by the scheme MOH + ROH ⇌ MOR + HOH.

•••• The cleavage of organosiloxanes may be accomplished with methyl alcohol also. In this case, an azeotropic mixture of the organomethoxysilane formed and the original alcohol is distilled from the reaction mixture as the lowest boiling component.

proceeding may be represented by the following general scheme:

$$\frac{1}{m}(R_nSiO_{2-0.5n})_m + (4-n)R'OH \xrightarrow[-0.5(4-n)H_2O]{R'OK} R_nSi(OR')_{4-n},$$

where: n = 1 – 3, m may be varied over wide limits and R represents similar or different hydrocarbon radicals.

The addition of an inert solvent, insoluble in water (toluene, benzene etc.), to the reaction mixture has a very advantageous effect. However, the addition of dehydrating agents gives better results than azeotropic distillation of water. The most convenient agents to use are the corresponding tetraalkoxysilanes and in most cases [apart from CH_3OH and $(CH_3)_2CHOH$] it is possible to use commercial ethyl silicate.* In the latter case, the water hydrolyzes the tetraethoxysilane by the scheme $Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH$, and the alcohol, liberated during the hydrolysis and also during transesterification, $Si(OC_2H_5)_4 + 4ROH \rightarrow Si(OR)_4 + 4C_2H_5OH$, may be distilled readily from the reaction mixture.

When tetraalkoxysilanes are used as the water-binding agents, the synthesis is achieved by the general scheme

$$\frac{1}{m}(R_nSiO_{2-0.5n})_m + (4-n)R'OH + (1-0.25n)Si(OC_2H_5)_4 \longrightarrow$$

$$\longrightarrow R_nSi(OR')_{4-n} + (4-n)C_2H_5OH + (1-0.25n)SiO_2$$

In this case, the yields of organoalkoxysilanes increase to 90 – 95%. By this metod it is also possible to synthesize alkoxy derivatives from alcohols with b.p. below 90 – 100°. However, the latter may also be obtained by the direct interaction of appropriate organosiloxanes and alkoxysilanes in the absence of alcohol [1, 2].

By the reactions of various alcohols containing 4 – 12 carbon atoms with hexamethylcyclotrisiloxane, octamethylsiloxanes or with a high-molecular linear polydimethylsiloxane (M = 200 – 400 thousand) we obtained 12 dimethyldialkoxysilanes, presented in the table. It should be noted that with the use of all the above polydimethylsiloxanes, the yields of the alkoxysilanes remained approximately the same. By interaction of the same alcohols with hexamethyldisiloxane, polymethylsesquisiloxane, $CH_3SiO_{1.5}$, or with phenylpolysesquisiloxane, $C_6H_5SiO_{1.5}$, we obtained 11 trimethylalkoxysilanes, 6 methyltrialkoxysilanes and 5 phenyltrialkoxysilanes, respectively, which are presented in the same table. Secondary alcohols reacted with organosiloxanes with much more difficulty than primary ones and we were quite unable to react tertiary ones under the conditions studied.

Siloxane polymers, containing phenyl radicals, which increase the electrophilic tendencies of the silicon atoms, are cleaved by alcohols more readily than polydialkylsiloxanes. The reactivity of the latter decreases in the series: $(R_2SiO) > R_3Si(OSiR_2)_nOSiR_3 > R_3SiOSiR_3 > RSiO_{1.5}$. It must be assumed that the minimal reactivity of $RSiO_{1.5}$ is caused primarily by its trimeric structure.

Polyorganohydroxysiloxanes react with alcohol with the formation of organotrialkoxysilanes by the scheme

$$\frac{1}{m}(RSiHO)_m + 3R'OH \xrightarrow{-KOH} RSi(OR')_3 + H_2O + H_2.$$

Thus, for example, by the reaction of polyethylhydroxysilane (GKZh-94) with n-butyl alcohol, we obtained ethyltributoxysilane.

The reaction mechanism for the formation of organoalkoxysilanes from organosiloxanes and alcohols may be represented by the following scheme:

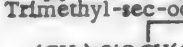
$$\geqslant Si\overset{\curvearrowright}{\underset{\uparrow}{O}}-Si\leqslant \rightleftharpoons \geqslant SiOR + \ddot{O}-Si\leqslant \qquad (5)$$
$$\quad \overset{\uparrow}{O}R^-$$

$$\geqslant SiO^- + ROH \rightleftharpoons \geqslant SiOH + RO^- \qquad (6)$$

$$\geqslant Si-OH + ROH \rightleftharpoons \geqslant SiOR + HOH \qquad (7)$$

* We have used tetraethoxysilane successfully for drying alcohol (in the presence of catalytic amounts of sodium ethylate).

Physical Constants, Analysis Data and Yields of Organoalkoxysilanes Synthesized

$R_nSi(OR')_{4-n}$	B.p. (pressure in mm)	d_4^{20}	n_D^{20}	Empirical formula	% Si		% C		% H		Yield (in %)
					calc.	found	calc.	found	calc.	found	
$(CH_3)_3SiO(CH_2)_3CH_3$ Trimethyl-n-butoxysilane	124° (760)	0.7774	1.3926	$C_7H_{18}OSi$	19.20	19.41, 19.09	57.47	—	12.40	—	50
$(CH_3)_3SiO(CH_2)_4CH_3$ Trimethyl-n-amoxysilane	149 (760)	0.7849	1.4000	$C_8H_{20}OSi$	17.52	17.58, 17.37	59.93	60.18, 60.30	12.57	12.70, 12.80	51
$(CH_3)_3SiO(CH_2)_5CH_3$ Trimethyl-n-hexoxysilane	171 (760)	0.7901	1.4056	$C_9H_{22}OSi$	16.11	16.20, 16.23	62.00	—	12.72	—	48
$(CH_3)_3SiO(CH_2)_6CH_3$ Trimethyl-n-heptoxysilane	190 (760)	0.7950	1.4107	$C_{10}H_{24}OSi$	14.91	14.82, 15.00	63.76	—	12.84	—	49
$(CH_3)_3SiO(CH_2)_7CH_3$ Trimethyl-n-octoxysilane	211 (760)	0.7993	1.4151	$C_{11}H_{26}OSi$	13.88	13.77, 13.85	65.27	—	12.95	—	50
$(CH_3)_3SiO(CH_2)_8CH_3$ Trimethyl-n-nonoxysilane	230 (760)	0.8032	1.4191	$C_{12}H_{28}OSi$	12.98	13.07, 13.11	66.59	—	13.04	—	44
$(CH_3)_3SiO(CH_2)_9CH_3$ Trimethyl-n-decyloxysilane	104 (5)	0.8066	1.4227	$C_{13}H_{30}OSi$	12.19	12.10, 11.97	67.75	67.96, 68.00	13.12	13.16, 13.29	46
$(CH_3)_3SiO(CH_2)_2CH(CH_3)_2$ Trimethyl-iso-amoxysilane	144 (760)	0.7896	1.3977	$C_8H_{20}OSi$	17.52	17.47, 17.55	59.93	—	12.57	—	45
$(CH_3)_3SiOCH(CH_3)(CH_2)_3CH_3$ Trimethyl-sec-hexoxysilane	156 (760)	0.7851	1.4022	$C_9H_{22}OSi$	16.11	16.07, 16.00	62.00	—	12.72	—	42
$(CH_3)_3SiOCH(CH_3)(CH_2)_5CH_3$ Trimethyl-sec-octoxysilane	190—191 (760)	0.7970	1.4140	$C_{11}H_{28}OSi$	13.88	13.78, 13.97	65.27	65.41, 65.59	12.95	12.89, 13.01	44
 Trimethylcyclohexoxysilane	170 (760)	0.8573	1.4318	$C_9H_{20}OSi$	16.29	—	62.72	63.10, 63.13	11.70	12.03, 12.05	24
$(CH_3)_2Si[O(CH_2)_3CH_3]_2$ Dimethyldi-n-butoxysilane	56 (2)	0.8431	1.4058	$C_{10}H_{24}O_2Si$	13.74	14.00, 14.15	58.77	58.46, 58.14	11.84	12.05, 12.13	52
$(CH_3)_2Si[O(CH_2)_4CH_3]_2$ Dimethyldi-n-amoxysilane	115 (21)	0.8445	1.4139	$C_{12}H_{28}O_2Si$	12.08	12.14, 12.29	62.01	62.19, 62.38	12.14	12.13, 12.19	67
$(Ch_3)_2Si[O(CH_2)_5CH_3]_2$ Dimethyldi-n-hexoxysilane	139 (16)	0.8458	1.4204	$C_{14}H_{32}O_2Si$	10.78	10.70, 10.96	64.55	—	12.38	—	54
$(CH_3)_2Si[O(CH_2)_6CH_3]_2$ Dimethyldi-n-heptoxysilane	160 (15)	0.8463	1.4254	$C_{16}H_{36}O_2Si$	9.73	9.58, 9.66	66.60	—	12.58	—	50
$(CH_3)_2Si[O(CH_2)_7CH_3]_2$ * Dimethyldi-n-octoxysilane	179 (15)	0.8470	1.4297	$C_{18}H_{40}O_2Si$	8.87	8.79, 8.61	68.29	68.37, 68.14	12.74	12.89, 12.63	53

$(CH_3)_2Si[O(CH_2)_8CH_3]_2$ *	152	(2)	0.848	1.4332	$C_{20}H_{44}O_2Si$	8.15	8.28, 8.63	69.70	69.59, 69.37	12.87	12.98, 12.77	51
Dimethyldi-n-nonoxysilane												
$(CH_3)_2Si[O(CH_2)_9CH_3]_2$ *	170	(1)	—	1.4363	$C_{22}H_{48}O_2Si$	7.54	7.59, 7.86	70.90	71.00, 70.89	12.98	13.09, 12.87	45
Dimethyldi-n-decyloxsilane												
$(CH_3)_2Si[O(CH_2)_{10}CH_3]_2$ *	196	(1)	—	1.4392	$C_{24}H_{52}O_2Si$	7.01	7.08, 7.15	71.93	72.05, 72.01	13.08	13.09, 13.15	44
Dimethyldi-n-undecyloxysilane												
$(CH_3)_2Si[O(CH_2)_{11}CH_3]_2$ *	206	(0.5)	0.8500	1.4418	$C_{26}H_{56}O_2Si$	6.55	6.56, 6.76	72.82	72.81, 73.00	13.16	13.05, 13.28	45
Dimethyldi-n-dodecyloxysilane												
$(CH_3)_2Si[OCH(CH_3)(CH_2)_5CH_3]_2$	145	(3)	0.8410	1.4259	$C_{18}H_{40}O_2Si$	8.87	8.96, 8.99	68.29	—	12.74	—	50
Dimethyldi-sec-octoxysilane												
$(CH_3)_2Si[O(CH_2)_2CH(CH_3)_2]_2$	81	(4)	—	1.4112	$C_{12}H_{28}O_2Si$	12.08	11.93, 12.27	62.01	62.00, 62.29	12.14	12.20, 12.00	52
Dimethyldi-iso-amoxysilane												
$(CH_3)_2Si[OCH(CH_2)_4CH_2]_2$*	149	(15)	0.9455	1.4580	$C_{14}H_{28}O_2Si$	10.95	11.10, 11.27	65.57	65.85, 65.93	11.00	11.11, 10.82	55
Dimethyldi-cyclohexoxysilane												
$CH_3Si[O(CH_2)_3CH_3]_3$	101	(2)	0.8769	1.4109	$C_{13}H_{30}O_3Si$	10.70	11.04, 11.09	59.49	59.69, 59.35	11.52	11.64, 11.68	20
Methyltri-n-butoxysilane												
$CH_3Si[O(CH_2)_4CH_3]_3$	115	(1)	0.8736	1.4199	$C_{16}H_{36}O_3Si$	9.22	9.37, 9.46	63.10	—	11.92	—	25
Methyltri-n-amoxysilane												
$CH_3Si[O(CH_2)_5CH_3]_3$	187	(15)	0.8698	1.4260	$C_{19}H_{42}O_3Si$	8.10	8.00, 8.25	65.84	—	12.21	—	27
Methyltri-n-hexoxysilane												
$CH_3Si[O(CH_2)_6CH_3]_3$	215	(15)	0.8680	1.4314	$C_{22}H_{48}O_3Si$	7.23	7.29, 7.38	67.98	67.90, 68.02	12.45	12.40, 12.51	26
Methyltri-n-heptoxysilane												
$CH_3Si[O(CH_2)_2CH(CH_3)_2]_3$	121—122	(5)	0.8661	1.4161	$C_{16}H_{36}O_3Si$	9.22	9.79, 9.84	63.10	63.35, 63.04	11.92	11.69, 11.87	28
Methyltri-iso-amoxysilane												
$CH_3Si[OCH(CH_3)(CH_2)_5CH_3]_3$	180	(2)	0.8610	1.4323	$C_{25}H_{54}O_3Si$	6.52	6.68, 6.78	69.70	69.78, 70.02	12.64	12.59, 12.43	25
Methyltri-sec-octoxysilane												
$C_2H_5Si[O(CH_2)_3CH_3]_3$	118	(9)	0.879	1.4151	$C_{14}H_{32}O_3Si$	10.16	10.03, 9.83	60.82	60.78, 61.00	11.67	11.74, 11.90	20
Ethyltri-n-butoxysilane												
$C_6H_5Si[O(CH_2)_3CH_3]_3$	140	(1)	—	1.4610	$C_{18}H_{32}O_3Si$	8.65	8.31, 8.73	66.62	66.53, 66.45	9.94	9.78, 10.06	47
Phenyltri-n-butoxysilane												
$C_6H_5Si[O(CH_2)_4CH_3]_3$ *	170	(1.5)	—	1.4583	$C_{21}H_{38}O_3Si$	7.66	7.73, 7.47	68.80	68.59, 68.37	10.45	10.75, 10.83	54
Phenyltri-n-amoxysilane												
$C_6H_5Si[O(CH_2)_2CH(CH_3)_2]_3$	172	(3)	0.9257	1.4589	$C_{21}H_{38}O_3Si$	7.66	7.69, 7.85	68.80	69.70, 69.66	10.45	10.90, 10.94	53
Phenyltri-iso-amoxysilane												
$C_6H_5Si[OCH(CH_3)(CH_2)_5CH_3]_3$	229—230	(4)	0.9027	1.4610	$C_{30}H_{56}O_3Si$	5.70	5.86, 6.04	73.11	73.02, 72.92	11.45	11.48, 11.71	37
Phenyltri-sec-octoxysilane												
$C_6H_5Si[OCH(CH_2)_4CH_2]_3$	196	(1)	1.0291	1.5032	$C_{24}H_{38}O_3Si$	6.98	6.97, 6.95	71.59	72.10, 72.39	9.51	9.99, 10.00	11
Phenyltricyclohexoxysilane												

* New compound

Coordination of the alkoxyl ion with the electrophilic silicon atom leads to rupture of the siloxane bond and the formation of an alkoxysilane and an $\equiv SiO$ ion. The latter, by reacting with alcohol, again liberates an alkoxyl ion and is converted into a silanol.• Together with further interaction of the silanol with alcohol (eq. 7), there is the possibility of an undesirable condensation of the silanol (reaction 8).

$$2\equiv SiOH \rightarrow \equiv SiOSi\equiv + H_2O \qquad (8)$$

EXPERIMENTAL

Starting reagents. All the starting organosiloxanes and tetraalkoxysilanes were described in a previous communication [1]. Polymethyl- and polyphenylsesquisiloxanes were obtained by hydrolysis of methyl- and phenyltrichlorosilane, respectively [15], and dried in vacuum at 80 – 100°. All the starting alcohols (besides n- and isobutyl and isoamyl) were preparations of the firms Shukhardt, Miller and Schering Kahlbaum. They were purified by distillation on a column over calcium metal (the higher alcohols in vacuum).

Synthesis procedure. Syntheses with continuous azeotropic distillation of water were carried out in a ground glass joint apparatus, consisting of a round-bottomed flask, fitted with a water trap with a tap, connected to a reflux condenser and a thermometer (in the vapor). A mixture of the organosiloxane with 1 – 10 mole% of an alcohol solution of KOH and a large portion of an inert solvent (benzene or toluene) was boiled until the isolation of water in the trap ceased and then the contents were distilled from the flask with a pear fractionating column (20 – 25 cm).

One of the reagents was always used in considerable excess and in the case of the synthesis of trimethylalkoxysilanes, this was usually hexamethyldisiloxane and no solvent was used. The latter is explained by the fact that, as a rule, the trimethylalkoxysilanes formed had boiling points close to the boiling points of the original alcohols and often formed azeotropic mixtures with them. Syntheses in which a tetraalkoxysilane was used as a dehydrating agent were carried out by distillation of a mixture of the latter with the organosiloxane and 1 – 10 mole % of an alcohol solution of KOH on a column or a pear fractionating column (20 – 30 cm).

The organosiloxanes isolated in both cases were purified by distillation on a column over metallic sodium at reduced or normal pressure. The silicon analysis procedure and the determination of the physical constants were described previously [16].

Dimethyl-n-amoxysilane. A mixture of 14.8 g (0.05 mole) of octamethylcyclotetrasiloxane, 52.9 g (0.6 mole) of n-amyl alcohol and 0.56 g (0.01 mole) of powdered KOH were boiled using a reflux condenser with a water trap until the evolution of water ceased (12 hours). During this time, 2.6 ml (72%) of water was collected in the trap. Fractional distillation of the reaction mixture yielded together with 20.5 g of the original alcohol, 31.2 g (67%) of dimethyl-n-amoxysilane with b.p. 218 – 225°, n_D^{20} 1.4140. After a second distillation on a column, the substance had the constants presented in the table.

Literature data [17]: b.p. 97° (9 mm), d_4^{20} 0.8444, n_D^{20} 1.41378.

Dimethyl-n-butoxysilane. a) A mixture of 22.3 g (0.1 mole) of hexamethylcyclotrisiloxane, 66.7 g (0.9 mole) of n-butyl alcohol, in which 0.3 g of metallic sodium had been dissolved, and 50 ml of benzene was boiled using a reflux condenser fitted with a water trap. Over a period of 12 hours, 1.9 ml (35%) of water was liberated. After removal of the solvent and excess alcohol, fractional distillation of the reaction mixture gave 30.9 g (62%) of dimethyl-n-butylsilane with b.p. 186 – 191°, n_D^{20} 1.4040. A second distillation of this on a column gave a substance with the constants presented in the table.

b) A mixture of 29.7 g (0.1 mole) of octamethylcyclotetrasiloxane, 74.1 g (1 mole) of n-butyl alcohol, 45.8 g (0.22 mole) of tetraethoxysilane and 0.2 g of metallic sodium was distilled on a column with an efficiency of 15 theoretical plates. This yielded 40.5 g (100%) of ethyl alcohol with b.p. 78 – 80°, 10.6 g of n.butyl alcohol with b.p. 117 – 118° and 70.1 g (86%) of dimethyldi-n-butoxysilane with b.p. 190 – 195°, n_D^{20} 1.4060. After a second distillation in vacuum it had b.p. 81° (15 mm), d_4^{20} 0.8432, n_D^{20} 1.4057.

• Equations (5) and (6) represent a scheme for the mechanism of the formation of silanols from siloxanes by the action of alcoholic alkali on them.

Literature data [17]: b.p. 80° (15 mm), d_4^{20} 0.8431, n_D^{20} 1.40548.

Trimethyl-n-amoxysilane. A mixture of 60.0 g (0.37 mole) of hexamethyldisiloxane, 44.1 g (0.5 mole) of n-amyl alcohol and 1.0 g of KOH was boiled for 12 hours using a reflux condenser fitted with a water trap. During this time, 3.2 ml of water (71%) was collected in the trap. Distillation of the reaction mixture on a column yielded 30.0 g of the original hexamethyldisiloxane and 40.9 g (51%, calculated on the original alcohol) of trimethyl-n-amoxysilane with b.p. 140 – 144°, n_D^{20} 1.4021. After a second distillation on a column over metallic sodium, the latter had the constants presented in the table.

Literature data [17]: b.p. 145 – 147°, d_4^{20} 0.7871, n_D^{20} 1.4010.

Methyltriisoamoxysilane. A mixture of 13.4 g (0.2 mole) of finely powdered polymethylsesquisiloxane, 79.4 g (0.9 mole) of isoamyl alcohol and 1.0 g of KOH was boiled for 18 hours using a reflux condenser fitted with a water trap. During this time, 3.2 ml of water was isolated. Fractional distillation of the filtered reaction mixture, first at normal pressure and then in vacuum gave 57.8 g of the starting alcohol with b.p. 129 – 131° and 16.7 g (28%) of methyltriisoamoxysilane with b.p. 110 – 112° (3 mm), n_D^{20} 1.4162. After a second distillation, it had the constants presented in the table.

Literature data [18]: b.p. 110 – 111° (3 mm), d_4^{20} 0.8670, n_D^{20} 1.4160.

Phenyltri-sec-octoxysilane. A mixture of 6.5 g (0.05 mole) of finely powdered polyphenylsesquisiloxane, 58.5 g (0.45 mole) of octanol-2, 25 ml of benzene and 0.3 g of KOH was boiled for 6 hours using a reflux condenser fitted with a water trap. During this time, 2.3 ml of water was collected. After removal of the solvent and excess alcohol (42.0 g, distilling at 179°), the residue was repeatedly fractionated in vacuum. The yield of phenyltri-sec-octoxysilane with b.p. 227 – 230° (2 mm) and n_D^{20} 1.4610 was 9.9 g (40%).

Literature data [18]: b.p. 214 – 215° (2 mm), d_4^{20} 0.9022, n_D^{20} 1.4610.

SUMMARY

A method was developed for synthesizing organoalkoxysilanes by cleavage of organosiloxanes with alcohols in the presence of alkaline catalysts. By this method we obtained 35 organoalkoxysilanes of the structure $R_n'-Si(OR)_{4-n}$, in which n = 1, 2 and 3, R' = CH_3 or C_6H_5 and R is a primary (normal or iso) or secondary alkyl radical, containing from 4 to 12 carbon atoms; 8 of these were synthesized for the first time. A scheme was proposed for the reaction mechanism.

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CLEAVAGE OF SILOXANES WITH HALOSILANES; NEW METHOD OF SYNTHESIZING ORGANOSILOXANES •

M. G. Voronkov and L. M. Chudesova

Institute of Silicate Chemistry, Academy of Sciences, USSR

The siloxane bond Si – O – Si in organosilicon compounds, which is normally characterized by its reactivity, is readily cleaved by the action of halides of aluminum [1 – 7], titanium [8], iron [9], boron [10 – 13] and phosphorus [14 – 17], thionyl chloride [18] and hydrogen chloride [19].

In the present work, which is a development of the investigations of one of us [1, 2, 7, 8, 17, 20 – 26] on the cleavage reactions of organosiloxanes by electro- and nucleophilic reagents, we demonstrated the possibility of cleaving the siloxane bond with halo- or organohalosilanes by the general scheme

$$(4-n)R_3SiOSiR_3 + R'_nSiX_{4-n} \rightleftarrows R'_nSi(OSiR_3)_{4-n} + (4-n)R_3SiX,$$

where n = 0 – 3, X is a halogen and R and R' are identical or different organic (both aliphatic and aromatic) or silicoorganic radicals, H, halogen etc. The reaction represented by this scheme is an equilibrium one.

Cleavage of organosiloxanes by halosilanes is catalyzed by electrophilic element halides (Lewis's acid) and above all, by ferric chloride. This new reaction offers the possibility of easy and simple synthesis of a whole series of different organosiloxanes (and also organohalosiloxanes), including some which were difficultly accessible up to now.

The mechanism of the cleavage of siloxanes by halosilanes in the presence of ferric chloride may be represented by the following scheme: •

$$R'_3SiX + FeX_3 \rightleftarrows R'_3Si^+ + FeX_4^-$$

$$R_3SiOSiR_3 + R'_3Si^+ \rightleftarrows (R_3Si)_2\overset{+}{O}{-}SiR'_3 \rightleftarrows R_3SiOSiR'_3 + R_3Si^+$$

The interaction of the silenium ions, R_3Si^+, thus formed, with the anion FeX_4^- leads to regeneration of the catalyst and the formation of a new halosilane.

$$R_3Si^+ + FeX_4^- \rightleftarrows R_3SiX + FeX_3$$

The latter may also be formed as a result of reaction with the original halosilane.

$$R_3Si^+ + R'_3SiX \rightleftarrows R_3SiX + R'_3Si^+ \text{ etc.}$$

• Presented May 14, 1958 at the symposium on organosilicon chemistry in Dresden (German Dem. Rep.). For preliminary communications see [25 and 26].

•• In our opinion, the catalytic cleavage of organosiloxanes by halides of phosphorus, titanium and other elements proceeds analogously.

TABLE 1

Physical Constants, Data From Molecular Weight Determinations and Analyses and Yields of Organosiloxanes Synthesized

No.	Organosiloxane	B. p. (pressure in mm)	d_4^{20}	n_D^{20}	Empirical formula	M		% Si		% C		% H		Yield (%)••	Starting reagents and their ratio•••
						calc.	found	calc.	found	calc.	found	calc.	found		
1	$(CH_3)_3SiOSi(C_2H_5)_3$ 1,1,1-Trimethyl-3,3,3-triethyldisiloxane	171—172° (763)	0.8110	1.4108	$C_9H_{24}OSi_2$	204.47	200.4, 214.3	27.47	27.36, 27.29	52.87	53.20, 53.36	11.83	12.09, 12.19	56	1 + 9 (2 : 1)
2	$(C_2H_5)_3SiOSi(C_2H_5)_3$ Hexaethyldisiloxane	232—234 (760)	0.8445	1.4340	$C_{12}H_{30}OSi_2$	246.55	256.8, 256.9	22.79	22.81, 23.07	58.46	58.51, 58.58	12.27	12.29, 12.25	58	1 + 9 (1 : 2.5)
3	$(n\text{-}C_3H_7)_3SiOSi(C_3H_7\text{-}n)_3$ Hexa-n-propyldisiloxane	285—287 (768)	—	1.4417	$C_{18}H_{42}OSi_2$	330.71	327.4, 326.0	16.99	17.07, 17.18	65.37	—	12.80	—	58	1 + 18 (1 : 2.5)
4	$CH_3(C_2H_5)_2SiOSi(C_2H_5)_3$ • Methylpentaethyldisiloxane	208—212 (760)	0.8331	1.4268	$C_{11}H_{28}OSi_2$	232.52	231.5, 242.4	24.16	24.31, 24.39	56.82	56.68, 56.98	12.14	12.19, 12.30	54	2 + 9 (1.5 : 1)
5	$C_6H_5(CH_3)_2SiOSi(CH_3)_3$ Pentamethylphenyldisiloxane	205—207 (760)	—	1.4610	$C_{11}H_{20}OSi_2$	224.46	228.2, 227.0	25.03	25.12, 25.29	58.86	—	10.79	—	52	1 + 10 (3 : 1)
6	$C_6H_5(C_2H_5)_2SiOSi(CH_3)_3$• 1,1,1-Trimethyl-3,3-diethyl-3-phenyldisiloxane	236 (750)	0.9125	1.4737	$C_{13}H_{24}OSi_2$	252.51	253.5, 250.4	22.25	21.57, 21.68	61.84	62.60, 62.70	9.58	9.80, 9.94	53	1 + 11 (3 : 1)
7	$(CH_3)_2Si[OSi(CH_3)_3]_2$ Octamethyltrisiloxane	152—153 (760)	0.8210	1.3850	$C_8H_{24}O_2Si_3$	236.54	233.4, 240.8	35.62	35.39, 35.32	40.62	40.46, 40.38	10.23	10.42, 10.52	34	1 + 19 (4 : 1)
8	$C_2H_5SiH[OSi(CH_3)_3]_2$• 1,1,1,5,5,5-Hexamethyl-3-ethyltrisiloxane	162—164 (753)	0.8337	1.3919	$C_8H_{24}O_2Si_3$	236.54	236.0, 238.4	35.62	35.54, 35.33	40.62	40.64, 40.49	10.23	10.45, 10.58	20	1 + 12 (3 : 1)
9	$(C_2H_5)_2Si[OSi(CH_3)_3]_2$ 1,1,1,5,5,5-Hexamethyl-3,3-diethyltrisiloxane	188.5 (762)	0.8389	1.4010	$C_{10}H_{28}O_2Si_3$	264.50	259.0, 275.9	31.85	31.65, 31.44	45.39	46.09, 46.12	10.67	10.72, 10.79	54	1 + 13 (3 : 1)
10	$CH_3(C_6H_5)Si[OSi(CH_3)_3]_2$ • 1,1,1,3,5,5,5-Heptamethyl-3-phenyltrisiloxane	232—234 (760)	0.9116	1.4435	$C_{13}H_{26}O_2Si_3$	298.62	286.6, 294.4	28.22	28.31, 28.46	52.29	54.42, 54.58	8.78	8.82, 8.92	30	1 + 14 (5 : 1)
11	$(CH_3)_3Si[OSi(CH_3)_2]_2OSi(CH_3)_3$ Decamethyltetrasiloxane	192—195 (760)	0.8536	1.3895	$C_{10}H_{30}O_3Si_4$	310.70	301.5, 311.8	36.16	36.21, 36.02	38.66	38.52, 38.81	9.73	9.71, 9.69	14	1 + 19 (4 : 1)
12	$Si[OSi(CH_3)_3]_4$ Tetrakistrimethylsiloxysilane	216—218 (754)	0.8675	1.3900	$C_{12}H_{36}O_4Si_5$	384.86	378.6, 378.8	36.49	36.24, 36.15	37.45	38.15, 38.38	9.43	9.73, 9.80	30	1 + 20 (6 : 1)
13	$(CH_3)_3Si(OSiHC_2H_5)_2OSi(CH_3)_3$ • 1,1,1,7,7,7-Hexamethyl-3,5-diethyltetrasiloxane	204—205 (756)	0.8702	1.3998	$C_{10}H_{30}O_3Si_4$	310.70	308.8, 303.5	36.16	36.09, 36.03	38.66	38.69, 38.77	9.73	9.89, 9.89	10	1 + 12 (3 : 1)
14	$(CH_3)_3Si[OSi(C_2H_5)_2]_2OSi(CH_3)_3$ • 1,1,1,7,7,7-Hexamethyl-3,3,5,5-tetraethyltetrasiloxane	245—250 (750)	0.8792	1.4134	$C_{14}H_{38}O_3Si_4$	366.81	364.2, 367.5	30.63	30.09, 30.06	45.84	46.07, 46.27	10.44	11.17, 10.69	22	1 + 13 (3 : 1)

• New compound.

•• On starting halosilane.

••• The figures indicate the numbers of the starting reagents in Table 2. Their molar ratio is given in brackets.

It should be noted that during the reaction, the catalyst is slowly incapacitated, as demonstrated by the following reactions:

$$R_3SiOSiR_3 + FeCl_3 \rightleftarrows R_3SiCl + R_3SiOFeCl_2^{\cdot} \longrightarrow R_3SiCl + OFeCl$$
$$2FeCl_3 \rightleftarrows FeCl_2 + Cl_2$$

Due to this it is necessary to replenish the gradually decomposing catalyst, whose total consumption reaches 5 – 8 mole%.

Another reaction mechanism,

$$R_3SiOSiR_3 + FeX_3 \rightleftarrows R_3SiOFeX_2 + R_3SiX$$
$$R_3SiOFeX_2 + R'_3SiX \rightleftarrows R_3SiOSiR'_3 + FeX_3$$

is less probable since the reaction is also catalyzed by such metal halides as $ZnCl_2$, for example, which are incapable of cleaving the siloxane bond under the given conditions.

We will illustrate the possible applications of the cleavage of organosiloxanes by halosilanes.

1. The synthesis of hexaorganodisiloxanes, containing various radicals, was accomplished according to the scheme

$$R_3SiOSiR_3 + R'_3SiX \rightleftarrows R_3SiOSiR'_3 + R_3SiX$$

In this way, for example, by the reaction of excess hexamethyldisiloxane with triethylchlorosilane, dimethylphenylchlorosilane or diethylphenylchlorosilane and also by the reaction of excess 1, 1, 3, 3-tetraethyl-1, 3-dimethyldisiloxane with triethylchlorosilane we obtained the corresponding hexaorganodisiloxanes (Table 1, substances 1, 5, 6 and 4) in yields of about 50%.

It should be noted that under the conditions we studied, organofluorosilanes apparently did not react with organosiloxanes. Thus, for example, we observed no reaction at all between hexaethyldisiloxane and tributylfluorosilane. Organohalosilanes (like aluminum, titanium and phosphorus halides) do not cleave hexachlorodisiloxane. Thus, when hexachlorodisiloxane was boiled for a long time with triethylchlorosilane in the presence of ferric chloride, no silicon chloride was formed. This may be explained by the considerable reduction in the polarity of the Si – O bond in OSi_2Cl_6 due to the I-effect of the chlorine atom, which leads to the oxygen atom losing its nucleophilic activity as is also confirmed by spectroscopic data [27].

2. The conversion of lower hexaorganodisiloxanes into higher ones or of higher triorganohalosilanes into lower ones proceeds by the scheme

$$R_3SiOSiR_3 + 2R'_3SiX \rightleftarrows R'_3SiOSiR'_3 + 2R_3SiX$$

Thus, for example, the interaction of hexamethyldisiloxane with excess triethylchlorosilane yielded hexaethyldisiloxane (yield 58%) and trimethylchlorosilane (yield 75%).

3. Chain lengthening of organosiloxanes was accomplished by the scheme

$$(n+1)R_3SiOSiR_3 + nR'_2SiX_2 \rightleftarrows R_3Si(OSiR')_nOSiR_3 + 2nR_3SiX$$

Thus, by the reaction of excess hexamethyldisiloxane with dimethyldibromosilane, together with 100% of trimethylbromosilane, we isolated octamethyltrisiloxane and decamethyltetrasiloxane in yields of 34 and 14%, respectively. The interaction of hexamethyldisiloxane with methylphenyldichlorosilane or with ethyldichlorosilane led to the formation of 3-phenylheptamethyltrisiloxane in 30% yield or 1, 1, 1, 5, 5, 5-hexamethyl-3-ethyltrisiloxane in 20% yield, respectively. The last two examples show that the starting reagents may contain aromatic radicals or hydrogen atoms at the silicon atom and that these are retained during the reaction.

4. The synthesis of branched organosiloxanes may be represented by the two following schemes:

$$3R_3SiOSiR_3 + R'SiX_3 \rightleftarrows R'Si(OSiR_3)_3 + 3R_3SiX,$$
$$4R_3SiOSiR_3 + SiX_4 \rightleftarrows Si(OSiR_3)_4 + 4R_3SiX.$$

However, these two reactions proceed with difficulty with the appropriate chlorosilanes. Thus, for example, ethyltrichlorosilane hardly reacts with hexamethyldisiloxane. On the other hand, phenyltrichlorosilane reacts with the latter, but not more than two chlorine atoms are replaced by $(CH_3)_3SiO$ groups. Bromo- and iodosilanes react quite readily in this direction. In particular, on reacting with hexamethyldisiloxane, tetrabromosilane forms tetrakis(trimethylsiloxy)silane in 30% yield. Branched organosiloxanes can also be obtained from siloxanes which already have a branched structure, for example, by reactions of trialkylhalosilanes with tetrakis-(trimethylsiloxy)--silane or with alkyltris(trimethylsiloxy)silanes.

It should be stated that the number of examples of the application of the cleavage of siloxanes by halosilanes does not stop here. This reaction may also be used for the synthesis of organohalosiloxanes (by the use of excess halosilanes), for the cleavage of cyclosiloxanes (which, incidentally, hardly occurs with chlorosilanes) etc.

The reactivity of the siloxane bond with respect to halosilanes decreases with a decrease in the electron donor properties of the oxygen atom, which are determined by the character of the substitutents at the silicon atoms. In accordance with this, R_3SiO groups react with halosilanes most readily, while R_2SiO groups [in $(R_2SiO)_n$ and $R_3Si(OSiR_2)_nR$] show considerably less reactivity and in the form of R_2SiCl_2 are hardly cleaved in reactions with chlorosilanes (but not bromo- and iodosilanes). Thus, for example, we observed no interaction of triethylchlorosilane with octaethyltrisiloxane, hexamethylcyclotrisiloxane or octamethylcyclotetrasiloxane. In the reaction of the latter with triethylbromosilane, 63% of dimethyldibromosilane was fromed.

The nature of the halogen atom also plays an essential role in the reaction of siloxanes with halosilanes. The reactivity of the latter increases considerably with a fall in the bond energy of the silicon and halogen atoms, i.e. in going from fluoro- to iodosilanes. As already mentioned, fluorosilanes hardly react with any organosiloxanes and chlorosilanes do not react with polydiorganosiloxanes, while bromo- and iodiosilanes cleave them.

By means of the cleavage of organosiloxanes with halosilanes, we synthesized 14 organosiloxanes of various structures, which are presented in Table 1; 6 of these compounds were previously unknown.

EXPERIMENTAL

Starting materials. The synthesis of hexamethyldisiloxane, hexaethyldisiloxane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane and tetrakis(trimethylsiloxy)silane was described previously [23]. 1, 3-Dimethyltetraethyldisiloxane was obtained by the reaction of sulfuric acid, containing traces of mercury sulfate, with methyldiethylsilane [28]. In its turn, the latter was obtained by the reaction of ethylmagnesium bromide with methyldichlorosilane. Dimethyl- and diethylphenylchlorosilanes were also obtained by the Grignard method from phenyltrichlorosilane. Triethylchloro- and triethylbromosilanes were obtained by cleavage of hexaethyldisiloxane with the appropriate aluminum halides [1]. Dimethyldibromosilane and tetrabromosilane were the reaction products of dimethyldiphenoxysilane and tetraphenoxysilane [29] with aluminum bromide. Octamethyltrisiloxane and octaethyltrisiloxane were obtained by cohydrolysis of a mixture of the appropriate trialkylchloro- and dialkyldichlorosilanes. Ethyldichlorosilane, ethyltrichlorosilane, diethyldichlorosilane, phenyltrichlorosilane and methylphenyldichlorosilane were the industrial products (the ethyltrichlorosilane was freed from traces of diethylchlorosilane by distillation over aluminum chloride). Tributylfluorosilane was described previously [24].

All the starting materials were purified mainly by distillation on a column. Their physical constants are presented in Table 2.

Synthesis procedure. All the syntheses were accomplished by slow distillation of a mixture of the appropriate siloxane (which was usually taken in excess) and the halosilane on a fractionating column with an efficiency of 15 theoretical plates. * During the distillation, the catalyst, powdered anhydrous ferric chloride, was gradually

* In all the syntheses, precautions were taken against the entrance of atmospheric moisture.

TABLE 2

Physical Properties of Starting Compounds

Sample No.	Compound	B. p. (pressure in mm)	d_4^{20}	n_D^{20}
1	$[(CH_3)_3Si]_2O$	100.4° (760)	0.7636	1.3774
2	$[CH_3(C_2H_5)_2Si]_2O$	90 (20)	0.8222	1.4192
3	$[(C_2H_5)_3Si]_2O$	236.3 (760)	0.8443	1.4340
4	$[(CH_3)_3SiO]_4Si$	69 (1.5)	0.8675	1.3892
5	$[(CH_3)_2SiO]_3$	134.6 (760)	M.p.	64.5°
6	$[(CH_3)_2SiO]_4$	175.8 (760)	0.9561	1.3968
7	$[(CH_3)_3SiO]_2Si(CH_3)_2$	152.5 (760)	0.8200	1.3849
8	$[(C_2H_5)_3SiO]_2Si(C_2H_5)_2$	138 (5)	0.893	1.4385
9	$(C_2H_5)_3SiCl$	146.5 (760)	0.8968	1.4313
10	$C_6H_5(CH_3)_2SiCl$	196.0 (760)	—	—
11	$C_6H_5(C_2H_5)_2SiCl$	230 (760)	—	—
12	$C_2H_5SiHCl_2$	75.0 (760)	—	—
13	$(C_2H_5)_2SiCl_2$	130.2 (760)	—	1.4309
14	$C_6H_5(CH_3)SiCl_2$	76.9 (10)	—	1.5190
15	$C_2H_5SiCl_3$	97.9 (760)	1.2386	1.4257
16	$C_6H_5SiCl_3$	201.1 (760)	1.324	1.5247
17	$(C_2H_5)_3SiBr$	164.5 (760)	1.145	1.4571
18	$(n\text{-}C_3H_7)_3SiBr$	214 (767)	—	—
19	$(CH_3)_2SiBr_2$	111.5 (760)	1.727	—
20	$SiBr_4$	152.8 (760)	M.p.	5.4°
21	$(C_4H_9)_3SiF$	225.3 (760)	0.8404	1.4238
22	$(C_2H_5)_3SiI$	191.2 (760)	1.352	1.4948
23	$Cl_3SiOSiCl_3$	137 (760)	—	—

introduced into the reaction mixture. After distillation of the organohalosilane formed and frequently, the excess starting organosiloxane also, a second fractional distillation of the still residue (in a series of cases it was filtered free from iron halides and oxyhalides) at normal or reduced pressure yielded the reaction products. In individual cases, the crude organosiloxane was washed with a solution of soda or alkali to remove traces of organohalosiloxanes and then with water and dried calcium chloride.

Due to the similarity of the procedures, we present a description of the most characteristic syntheses. Data on the other experiments may be obtained from Table 1.

All the analyses of the organosiloxanes obtained were carried out by Yu. N. Platonov, to whom we are grateful.

Synthesis of 1, 1, 1,-trimethyl-3, 3, 3-triethyldisiloxane. A mixture of 30.2 g (0.2 mole) of triethylchlorosilane, 48.7 g (0.3 mole) of hexamethyldisiloxane and 0.2 g of anhydrous ferric chloride was distilled on a column. During the distillation, a further 1.0 g of $FeCl_3$ was gradually added. At 56.5 – 58.5°, 17.1 g (79%) of trimethylchlorosilane with n_D^{20} 1.3885 distilled. Further distillation gave 21.1 g (0.13 mole) of the original hexamethyldisiloxane with b.p. 98 – 100°, n_D^{20} 1.3785 and 23.0 g (66%, calculated on the hexamethyldisiloxane reacting) of 1, 1, 1-trimethyl-3, 3, 3-triethyldisiloxane with b.p. 170 – 174°, n_D^{20} 1.4115. After a second distillation, it had the constants presented in Table 1.

Literature data [30]: b.p. 172° (724 mm), d_4^{20} 0.8110, n_D^{20} 1.4105.

Preparation of hexaethyldisiloxane and trimethylchlorosilane. A mixture of 32.5 g (0.2 mole) of hexamethyldisiloxane, 75.4 g (0.5 mole) of triethylchlorosilane and 0.2 g of $FeCl_3$ was distilled on a column with the gradual addition of a further 1.4 g of catalyst. As a result, we obtained 32.7 g (75%) of trimethylchlorosilane with b.p. 57.0 – 59.5°, n_D^{20} 1.3885; 19.2 g (0.13 mole) of the original triethylchlorosilane with b.p. 146 – 147° and 26.5 g (54%, calculated on the original hexamethyldisiloxane) of hexaethyldisiloxane with b.p. 86 – 88° (5 mm), n_D^{20} 1.4340. After a second distillation, the last substance had the constants presented in Table 1.

Literature data [20]: b.p. 236.3° (760 mm), d_4^{20} 0.8443, n_D^{20} 1.4340.

Synthesis of 1, 1, 1, 5, 5, 5-hexamethyl-3, 3-diethyltrisiloxane. A mixture of 31.4 g (0.2 mole) of diethyldichlorosilane, 97.4 g (0.6 mole) of hexamethyldisiloxane and 0.2 g of ferric chloride was distilled on a column. During the distillation, a further 1.6 g of $FeCl_3$ was added. At 57 – 59°, 36.3 g (83.5%) of trimethylchlorosilane with n_D^{20} 1.3885 distilled. Further distillation yielded 39.1 g (0.24 mole) of unreacted hexamethyldisiloxane with b.p. 98 – 100°, n_D^{20} 1.3793. Distillation of the filtered residue gave 25.8 g (54%, calculated on the hexamethyldisiloxane reacted) of hexamethyl-3, 3-diethylsiloxane with b.p. 185 – 193°, n_D^{20} 1.4015.

Literature data [31]: b.p. 187° (733 mm), d_4^{20} 0.8389, n_D^{20} 1.4005.

From the high-boiling residue we isolated 11.8 g (32%) of hexamethyl-3, 3, 5, 5-tetraethyltetrasiloxane with b.p. 245 – 260°, n_D^{20} 1.4135, which had the constants presented in Table 1 after a second distillation.

Preparation of tetrakis (trimethylsiloxy)silane. A mixture of 97.4 g (0.6 mole) of hexamethyldisiloxane, 34.8 g (0.1 mole) of silicon bromide and 0.3 g of ferric chloride was distilled on a column. During the reaction, a further 1.5 g of $FeCl_3$ was introduced. 40.4 g (66%) of trimethylbromosilane with b.p. 78 – 81° and 36.5 g (0.225 mole) of unreacted hexamethyldisiloxane distilled. The residue in the distillation flask with b.p. over 190° (29.1 g) was filtered, washed with water, 5% KOH solution and again with water and dried over $CaCl_2$. Subsequent disti distillation of it over sodium metal gave 11.5 g (30%) of tetrakis(trimethylsiloxy)silane with b.p. 218 – 224°, n_D^{20} 1.3904, which had the constants presented in Table 1 after a second distillation.

Literature data [31]: b.p. 220° (733 mm), d_4^{20} 0.8677, n_D^{20} 1.3895.

In addition, we also obtained about 2 g of a substance with b.p. 295 – 305°, which solidified in the tube of the condenser on distillation, and was apparently hexakis(trimethylsiloxy)disiloxane.

SUMMARY

The possibility of cleaving siloxane bonds in organosiloxanes with halosilanes in the presence of electrophilic catalysts was demonstrated. This reaction, which is a rearrangement of Si – O – Si and Si – X bonds (X = halogen), is a new, simple and convenient method of synthesizing various organosiloxanes. This method was used for synthesizing 14 compounds of this type, of which 6 were previously unknown. A scheme for the reaction mechanism is presented.

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STUDY OF THE ISOMERIC CONVERSIONS OF ALKYLNAPHTHALENES

I. ISOMERIZATION OF MONOMETHYLNAPHTHALENES

N. N. Vorozhtsov Jr. and V. A. Koptyug

D. I. Mendeleev Chemico-Technological Institute, Moscow

Isomeric conversions of alkyl- and arylnaphthalenes have been studied comparatively little up to the present time. By passing 1-methylnaphthalene over silica gel at 420° in a stream of nitrogen, Mayer and Schiffner [1] obtained a small amount of the 2-isomer. Similarly, 2-ethylnaphthalene was obtained from 1-ethylnaphthalene. Apparently, under these conditions, 1, 6-dimethylnaphthalene was converted into the 2, 6-isomer, which was obtained in 20% yield. Later, Cullinane and Chard [2] carried out experiments on the isomerization of 1-methylnaphthalene over synthetic aluminosilicate (1 : 2) at 450°. According to their data, the monomethylnaphthalene fraction (yield 45%), obtained by distillation of the catalyzate, contained only the 2-isomer. Together with 2-methylnaphthalene, under these conditions considerable amounts of naphthalene and dimethylnaphthalenes (yields 19.5 and 7%, respectively) were formed. According to patent data [3], monoethylnaphthalenes may be isomerized by passage over $MgO - Al_2O_3$ catalyst at 425°. At equilibrium, the monoethylnaphthalene fraction contained 20% of the 1- and 80% of the 2-isomer. The simultaneous passage of hydrogen chloride increased and maintained the isomerizing capacity of the catalyst. By heating 1-sec.-butylnaphthalene with activated gumbrime at 300°, Gavrilov and Nikitina [4] obtained a complex mixture of substances, in which 1- and 2-sec.-butylnaphthalenes were present in approximately equal amounts. Interesting results were obtained by Japanese chemists [5], who studied the isomerization of a series of naphthalene derivatives in the liquid phase in the presence of aluminum chloride. They reported great ease of isomeric conversions in the case of 1- and 2-benzylnaphthalenes. Thus, under the action of aluminum chloride (0.075 mole per mole of hydrocarbon) in chlorobenzene solution at 0°, the equilibrium ratio of isomers was reached after only 30 minutes. Here the monobenzylnaphthalene fraction contained 10% of the 1- and 90% of the 2-isomer. The isomerization was accompanied by the formation of naphthalene. In contrast to monobenzylnaphthalenes, monomethylnaphthalenes were not isomerized, even when heated to 50° with an equimolecular amount of aluminum chloride.

In the field of arylnaphthalene isomerization, it is only known that 1-phenylnaphthalene is converted into 2-phenylnaphthalene when passed over silica gel at 350° [1]; 1-(o-hydroxyphenyl)-naphthalene gives the 2-isomer when passed over a dehydrogenating chromium catalyst [6] and 1, 1'-dinaphthyl is isomerized into 2, 2'-dinaphthyl when boiled with aluminum chloride in carbon disulfide [7].

We made a study of isomerization of monomethylnaphthalenes on a synthetic aluminosilicate catalyst in the temperature range 270 – 450° with a stream of hydrogen chloride and without it. The results thus obtained show that contrary to the data of [2], the conversion of 1-methylnaphthalene into the 2-isomer is a reversible process. The reversibility of the isomerization was demonstrated by the isolation of 1-methylnaphthalene (in the form of the molecular compound with 2, 4, 7-trinitrofluorenone see [8]) from a catalyzate obtained by catalytic treatment of 2-methylnaphthalene (Exp. 5). At equilibrium, according to the solidification point (see [9]), the monomethylnaphthalene fraction contained approximately 30% of the 1- and 70% of the 2-isomer and the position of the equilibrium was hardly affected by a change in temperature (cf. Experiments 1, 4 and 6). In Experiment 1, which was carried out under conditions identical with those of Cullinane and Chard's experiment [2], the monomethylnaphthalene fraction had approximately the same composition. In accordance with the data of these investigators, the isomerization of 1-methylnaphthalene at 450° was accompanied by the formation of considerable amounts of naphthalene: the yield of the naphthalene fraction was 24.3% of the weight of the catalyzate. Since

it is known that the activation energy for disproportionation is considerably greater than the activation energy for isomerization [10, 11], it might be expected that lowering the temperature would suppress the formation of naphthalene and high-boiling products, apparently containing di- and polymethylnaphthalenes. Actually, at the same 1-methylnaphthalene through-put rate, the yields of the naphthalene fraction at 350 and 310° were 14.5 and 5.2%, respectively. Increasing the input rate of the methylnaphthalene to be isomerized also led to a fall in the naphthalene fraction yield (cf. Experiments 3 and 4, and 6 and 7). The same rule was observed for the yield of the high-boiling products (di- and polymethylnaphthalenes) and the products of cracking (fractions from ~70 to 210°). The decrease in the yield of disproportionation products, observed when the contact temperature was lowered, led to a sharp increase in the yield of monomethylnaphthalenes from 34.3% at 450° to 68% at 310°. As follows from experiments 1, 2 and 9, 1-methylnaphthalene is also isomerized smoothly in the absence of hydrogen chloride, but at a slightly lower rate (cf. Experiments 7 and 9). The ease of the isomeric conversions of methylnaphthalene in the presence of an aluminosilicate catalyst attracts attention. Thus, in experiment 8, catalytic treatment of 1-methylnaphthalene in a stream of hydrogen chloride at a temperature of 270° only yielded a fraction of monomethylnaphthalenes containing 61% of the 2-isomer. This observation is unexpected if we consider that in previous work the isomerization of alkylnaphthalenes was carried out at 420 – 450° [1 – 3] and also that methylnaphthalene is not isomerized under the action of such strong catalysts, • as aluminum chloride [5].

The results obtained show that the optimal temperature for the isomerization of monomethylnaphthalenes on an aluminosilicate catalyst should be considered as the range 300 – 350°. At 320°, it is possible to pass at least 140 g of 1-methylnaphthalene over 1 liter of catalyst in 1 hour. In this case, the yield of the monomethylnaphthalene fraction reaches 75% (calculated on the 1-methylnaphthalene passed) with 60% of the 2-isomer in the fraction. The side reaction of disproportionation, leading to the formation of naphthalene and polymethylnaphthalenes, is then of secondary importance.

As is known [12], the fraction of monomethylnaphthalenes isolated from coal tar contains approximately equal amounts of 1- and 2-isomers. Part of the 2-methylnaphthalene can be isolated by freezing out. The separation of the residual mixture, containing 20 – 25% of the 2-isomer, requires complex methods [9, 12]. The data we obtained indicates the possibility of using this mixture for the preparation of 2-methylnaphthalene.

EXPERIMENTAL

1-Methylnaphthalene was obtained from 1-chloromethylnaphthalene [13] (m.p. 29 – 31° through the organomagnesium compound by the procedure in [14]; the yield was 71%, the b.p. (after a second distillation) 241.5 – 243.0° and n_D^{20} 1.6174. According to [15], 1-methylnaphthalene has b.p. 244.6°, n_D^{20} 1.6174.

2-Methylnaphthalene. The technical product, purified by recrystallization from methyl alcohol, was used. The m.p. was 34.5 – 35°. M.p. 34.4° is reported in the literature [16] for 2-methylnaphthalene.

Isomerization of monomethylnaphthalenes. The catalyst was placed in a vertical quartz tube (17 mm diameter), heated with an electric furnace. The catalyst bed (~38 cm high) was between two layers of broken porcelain, the upper of which served to evaporate the methylnaphthalene, added at a constant rate from a graduated cylinder with nitrogen. The upper end of the catalyst tube had an inlet for hydrogen chloride and the lower one was connected to a receiver for the catalyzate. The isomerization catalyst used was tablets of synthetic aluminosilicate, containing 30% of aluminum oxide, 65.5% of silicon oxide and 0.5% of iron oxide. The catalyzate was dissolved in ether. The ether solution was washed with water and dried with anhydrous calcium chloride. The residue after removal of the ether was fractionated on a column with an electrical heater, filled with glass rings, 4 mm in diameter and 0.5 mm high (the height of the packing was 400 mm). The monomethylnaphthalene fraction thus obtained (b.p. 237 – 243°) was again rectified, when the bulk of it boiled in the range 239 – 241°. The solidification point of the fraction with b.p. 239 – 241° was determined and from this we found (see [9]) the ratio of 1- and 2-methylnaphthalenes. In all the experiments, the amount of catalyst was 55 g; the operating time of the catalyst was 2 – 3 hours; the rate of hydrogen chloride through-put was 50 ml/min. The catalyst was regenerated by heating in the catalyst tube in a stream of air for 2.5 hours at 500 – 520°. In all, 30 – 40 g of methylnaphthalene was passed in each experiment, except Experiment 9, where twice the amount of 1-methylnaphthalene was used. The results of the experiments are presented in the table. In Experiments 2 – 9, the catalyzates were yellowish liquids with a green fluorescence. In Experiment 1, naphthalene crystallized from the catalyzate at room temperature.

• Under the action of aluminum chloride, the isomerization of chloronaphthalene proceeds quite rapidly even at 20° [5].

Experiment No.	Methylnaphthalene isomer	Temperature	Rate of methylnaphthalene put (g/hour)	Catalyzate yield (% of weight of methylnaphthalene passed)	Yield of fractions • (% of catalyzate weight)				Solidification pt. of fraction of monomethylnaphthalenes after a sec. distillation (b.p. 239 – 241°)
					up to 210°	215-225°	237-243°	still residue	
1••	1-	450°	5.8	60.0	11.2	24.3	34.3	23.6	12.2
2••	1-	350	13.9	88.0	0.9	7.2	65.5	15.5	12.5
3	1-	350	18.0	94.5	2.2	8.1	60.7	10.6	13.4
4	1-	350	5.8	85.0	3.4	14.5	47.3	20.0	13.9
5	2-	350	5.6	87.5	4.0	11.9	43.5	17.5	12.3
6	1-	310	5.8	91.5	1.5	5.2	68.0	11.8	14.5
7	1-	310	17.2	94.5	0.5	3.0	71.5	7.7	9.2
8	1-	270	5.7	85.5			71.5		7.5
9••	1-	320	12.0	92.8	1.2	3.8	79.2	6.3	6.5

• The yields of the intermediate fractions are omitted.

•• Experiments 1, 2 and 9 were carried out in the absence of hydrogen chloride.

Experiment 5. We isolated 2.4 g of 2-methylnaphthalene with m.p. 31.5 – 33.0° from 8.9 g of the redistilled fraction of monomethylnaphthalenes (solidification point +12.3°, n_D^{20} 1.6120) by freezing it at -15°. The residual liquid mixture of 1- and 2-methylnaphthalenes was dissolved in 5 ml of anhydrous alcohol and the solution cooled to -30°. As a result, 0.9 g of 2-methylnaphthalene crystallized and was collected on a Buchner funnel, cooled to -50°. Subsequent cooling of the filtrate to -40, -50 and -60° yielded a further 1.9 g of 2-methylnaphthalene. The alcohol was distilled from the residual alcohol solution and the residue treated with a boiling solution of 8.6 g of 2, 4, 7-trinitrofluorenone in 50 ml of glacial acetic acid. Cooling the reaction mixture deposited an orange precipitate of the molecular compound. The weight was 9.16 g and the m.p. 140 – 151°. After recrystallizing this precipitate five times from glacial acetic acid, we obtained 2.02 g of orange needles with m.p. 162 – 163.3°. A mixed melting point with the molecular compound obtained from authentic 1-methylnaphthalene (m.p. 163 – 164°) was not depressed. For the molecular compound of 2, 4, 7-trinitrofluorenone with 1-methylnaphthalene, m.p. 163 - - 164° is reported in the literature [8] and m.p. 124.6 – 126° [17] for the compound with 2-methylnaphthalene.

Experiment 9. Passing 34.5 g of 1-methylnaphthalene steadily over the catalyst for 3 hours at a temperature of 320° yielded 32.6 g of a light yellow liquid with a solidification point of -1°. After regeneration of the catalyst, a further 37.8 g of 1-methylnaphthalene was passed through under the same conditions. The catalyzate obtained (yield 34.6 g) had solidification point +1°. Fractionation of the combined catalyzates yielded the following fractions: 1st b.p. 190 – 215°, 0.79 g; 2nd 215 – 225°, 2.53 g; 3rd 225 – 230°, 1.68 g; 4th 230 – 237°, 2.12 g; 5th 237 - - 243°, 53.12 g. The still residue weighed 4.25 g. Fractions 2 and 3 were crystalline pastes. Filtration of them yielded 0.78 and 0.48 g, respectively, of naphthalene with m.p. 64 – 70°. After recrystallization from methanol, the melting point rose to 78.5 – 79.5°. A mixed melting point with an authentic sample of naphthalene was not depressed. The first and fourth fractions were colorless liquids. Fraction 5 (solidification point +5.0°) was redistilled. The yield of the fraction with b.p. 239 – 241.5° (n_D^{20} 1.6125, solidification point +6.5°) was then 45.3 g. Judging by the solidification point [9], the fraction with b.p. 239 – 241.5° contained 40% of 1- and 60% of 2-methylnaphthalene. The addition of 3.16 g of pure 2-methylnaphthalene to 6.78 g of this fraction raised the solidification point to +16.2°. This rise corresponds to the value expected from the melting point diagram of mixture of 1- and 2-methylnaphthalenes.

Cooling 7.72 g of the fraction with b.p. 239 — 241.5° to 0° yielded 1.50 g of 2-methylnaphthalene with m.p. 31.5 – 32.5°. A mixed melting point with authentic 2-methylnaphthalene was not depressed. Treatment of 100 mg of the 2-methylnaphthalene obtained with 150 mg of 1, 3, 5-trinitrobenzene in 2 ml of alcohol yielded 200 mg of lemon yellow needles with m.p. 123.0 – 123.7°. M.p. 123 and 124° are reported in the literature [8] for the molecular compound of 1, 3, 5-trinitrobenzene with 2-methylnaphthalene. A mixed melting point of the substance obtained with authentic 1, 3, 5-trinitrobenzeneate of 2-methylnaphthalene was not depressed.

SUMMARY

1. It was shown that when 1-methylnaphthalene was passed over an aluminosilicate catalyst at 270 – 450° with a stream of hydrogen chloride and without it, it was converted into a mixture of 1- and 2-methylnaphthalenes. To some extent, the disproportionation of 1-methylnaphthalene occurred as a side reaction with the formation of naphthalene and high-boiling products (di- and polymethylnaphthalenes). The optimal temperature for the isomerization of 1-methylnaphthalene into the 2-isomer was the range 300 – 350°. At 320° and a 1-methylnaphthalene input rate of 140 g/hour per liter of catalyst, the yield of the monomethylene fraction, containing 60% of the 2-isomer, was 75%.

2. Conversion of 1-methylnaphthalene into the 2-isomer is a reversible process. At equilibrium, the monomethylnaphthalene fraction contains about 70% of the 2-isomer.

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INVESTIGATIONS IN THE FIELD OF SYNTHESIS AND CONVERSIONS OF SUBSTITUTED VINYL ETHERS

IX. FORMATION AND NATURE OF RESINOUS PRODUCTS OBTAINED IN THE VINYLATION OF PHENOLS

M. F. Shostakovskii, E. P. Gracheva and N. K. Kul'bovskaya

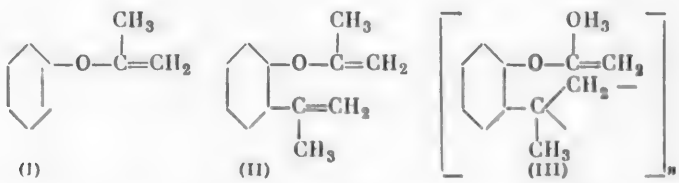
Institute of Organic Chemistry, Academy of Sciences, USSR

The vinylation of phenols by the Favorskii-Shostakovskii method for the preparation of vinyl aryl ethers, has been studied in a series of works [1 – 3]. Together with the corresponding ethers, a considerable amount of resinous products was always obtained by investigators. In the present work, we studied the nature of the products on the example of the resin obtained in the reaction of methylacetylene with phenol [3].

From literature data it is known that in the absence of polar solvents (water and methanol) it is not possible to isolate vinyl aryl ethers; low condensation polymers are obtained [1, 4]. The action of acetylene on p-alkylphenols in the presence of zinc or cadmium salts yields alkylphenol–acetylene resins [2, 5, 6]. Tert - Butylphenol--acetylene resin is known under the name of Coresin and several formulas have been proposed for it, though these have not been definitely proved [2, 4, 5, 7, 8]. The investigators rejected a polyvinyl structure for Coresin since infrared spectra and chemical data showed the presence of hydroxyl groups [9].

The resinous products obtained in the vinylation of phenols with methylacetylene in the presence of potassium hydroxide and water [3] differ from alkylphenol–acetylene resins in external appearance and properties. The latter appear as solid, friable resins, which do not distill in vacuum, and the average molecular weight of Coresin equals 800 – 1100. The resin formed in the vinylation of phenol with methylacetylene is a liquid which partly distills in vacuum and whose greatest molecular weight equals 500; the amount of resin formed during vinylation depends on the ratio of methylacetylene to phenol. With an increase in the amount of methylacetylene, the resin yield increases.

A study of the composition of the distillable fractions of resin by chemical and spectroscopic methods showed that it was a mixture of products (I – III).



(I) (II) (III)

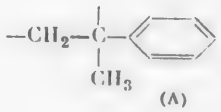
A fraction boiling at 110 – 115° (3 mm) was o-isopropenylphenyl isopropenyl ether (II), as shown by elementary analysis, hydrolysis, molecular refraction determination and spectral analysis. Fractions boiling at higher temperatures were mixtures of monomer (II) and polymer (III) with various degrees of polymerization.

We attempted to prepare o-isopropenylphenyl isopropenyl ether (II) by synthesis, starting from o-isopropenylphenol and methyl acetylene. The resinous products obtained in the vinylation of o-isopropenylphenol were found

to be identical with resins from experiments with phenol. However, it was found that when heated with alkali, o-isopropenylphenol decomposed to phenol and a resinous residue. The phenol liberated was evidently vinylated further and this secondary process prevented the synthesis from giving unequivocal results.

The infrared spectra • of the fractions were plotted in the region of 2.5 – 15 mμ. The spectrum in the region 2.5 – 3.5 mμ was plotted separately with high resolution and the ultraviolet spectrum was plotted in the region 230 – 350 mμ. The infra red spectra of fractions with b.p. 110 – 115°, 160 – 180° and 180 – 200° at 3 mm showed the absorption bands of a benzene ring and methyl, methylene and CH-aromatic groups and also the absorption bands of C=C bonds and C – O groups; the intensity of the absorption band caused by the double bond was much higher in the spectrum of the sample with b.p. 110 – 115° (3 mm) than the intensity of the double bond absorption bands in samples with b.p. 160 – 180° and 180 – 200° (3 mm). The partial overlap of the absorption bands of the benzene ring and the C=C double bond, due to the low resolving power of the apparatus, did not allow an accurate determination of the increase in intensity of the double bond absorption band of the fraction with b.p. 110 – 115° (3 mm) in comparison with a sample of isopropenyl phenyl ether.

The ultraviolet spectra of the samples showed a strong absorption band at 254 mμ and a considerably weaker band in the region of 290 mμ for the fraction with b.p. 110 – 115° (3 mm). Comparison of the ultraviolet spectrum of the fraction with the spectrum of α-methylstyrene [10] made it possible to ascribe the absorption bands at 254 and 290 mμ to an isopropenyl group attached to a benzene ring. For the fractions with b.p. 160 – 180° and 180 – 200° (3 mm), the absorption band at 254 mμ was weakened considerably and a new band at 285 mμ appeared, which could be ascribed to group (A).



(A)

On the basis of spectroscopic data, we may conclude that the fraction with b.p. 110 – 115° (3 mm) contains molecules of o-isopropenylphenyl isopropenyl ether (II) and the higher boiling fractions contain polymer molecules (III) with a certain amount of the monomeric form.

Comparison of the spectra of samples of o-isopropenylphenyl isopropenyl ether with the spectra of a series of disubstituted benzenes showed that the substituents were most probably in the ortho-position of the benzene ring.

EXPERIMENTAL

The experiments were carried out in rotating autoclaves, fitted with automatic heating and a remote manometer. The autoclave was cooled with dry ice for loading with methylacetylene. The methylacetylene was prepared according to the method in [11] and condensed in traps in dry ice.

1. Interaction of phenol with methylacetylene. Into an autoclave of 1 liter capacity were loaded 80 g of phenol, 45 g of potassium hydroxide, 23 ml of water and 136 g of methylacetylene. The reaction mixture was heated for 4 hours at 220°. The maximum pressure was 95 atm. and the final one, 44 atm. From the cooled autoclave, we collected 20 g of methylacetylene in a trap placed in dry ice. The product was steam distilled. 90 g of isopropenyl phenyl ether (I) was collected. Drying over $CaCl_2$ and distillation yielded 65.6 g (57%) of ether with b.p. 53.5 – 54° (11 mm), n_D^{20} 1.5050 [3]. The residue after the steam distillation was transferred to a separatory funnel, the upper resinous layer separated and the residue extracted with diethyl ether. The extract obtained was combined with the bulk of the resinous product. The ether solution was washed with potassium hydroxide solution and water, dried over potassium carbonate, filtered and the ether removed. We obtained 55 g (37%) of a brown, liquid resin. Vacuum distillation yielded the following fractions:

1st b.p. 50 – 100° (3 mm), n_D^{20} 1.5030, 14.1 g; 2nd b.p. 110 – 120° (3 mm), n_D^{20} 1.5370, 10.1 g; 3rd b.p. 120 – 160° (3 mm), n_D^{20} 1.5401, 6.7 g; 4th b.p. 160 – 180° (3 mm), n_D^{20} 1.5445, 3.8 g and the 5th b.p. 180 – 200° (3 mm), n_D^{20} 1.5520, 5.2 g. The residue was 13.5 g of a solid brown mass; M 450, 460.

• The UV- and IR-spectra were plotted in the optical laboratory of the Institute of Organic Chemistry, Academy of Sciences, USSR by B. V. Lopatin and we are very grateful to him for this.

The first fraction were light yellow and the last ones thick yellow polymers. A second distillation of the second fraction gave 5 g of o-isopropenylphenyl isopropenyl ether (II):

b.p. 110 – 115° (3 mm), d_4^{20} 1.0032, n_D^{20} 1.5370, MR_D 54.21; Calc. 54.72.

Found %: C 82.96, 82.80; H 8.52, 8.44. M 190.1, 193.0 $C_{12}H_{14}O$. Calculated %: C 82.73; H 8.10 M 174.2.

The alkaline solution, remaining after extraction with ether, was acidified to liberate a phenol layer, which yielded 2 g of phenol on distillation.

2. Hydrolysis of o-isopropenylphenyl isopropenyl ether. A sample of the ether (1–2 g) was placed in an ampule (150 ml) with 10 ml of butanol. 80 ml of 0.5 n $NH_2OH \cdot HCl$ solution (pH 2.9) was added. The mixture was boiled with shaking for 10 hours [12]. The acid liberated was titrated to Methyl Orange with 0.1 N NaOH. The calculations were based on the formula presented previously [3]. The amount of ether determined equalled 34.4 and 33.7%.

3. Interaction of o-isopropenylphenol with methylacetylene. o-Isopropenylphenol, obtained by the procedure in [13], had the following constants: b.p. 99 – 100° (22 mm), 85.6 – 86.5° (13 mm), n_D^{20} 1.5510. Into a 250 ml autoclave were placed 50 g of o-isopropenylphenol, 30 g of methylacetylene, 21 g of potassium hydroxide and 11 ml of water. The reaction mixture was heated at 220° for 3.5 hours. The product was steam distilled. After being dried over potassium carbonate, the liquid distillate was vacuum distilled. We obtained 6.1 g (12%) of isopropenyl phenyl ether with b.p. 57 – 60° (13 mm), d_4^{20} 1.9542, n_D^{20} 1.5049 [3]. By the method described above, the residue after the steam distillation yielded 35 g (54%) of a brown resin, from which the following fractions were obtained:

1st b.p. 90 – 110° (3 mm), n_D^{20} 1.5165, 10.1 g; 2nd b.p. 115 – 135° (3 mm), n_D^{20} 1.5406, 2.8 g; 3rd b.p. 135 – 180° (3 mm), n_D^{20} 1.5571, 1.0 g. The residue was 20.4 g of a solid brown resin.

A second distillation of the second fraction yielded 0.5 g of o-isopropenylphenyl isopropenyl ether:

b.p. 110 – 112° (3 mm), n_D^{20} 1.5365, d_4^{20} 1.0028.

Found %: C 82.12, 82.13; H 8.40, 8.58. $C_{12}H_{14}O$. Calculated %: C 82.73; H 8.1.

Acidification of the alkaline solution yielded a phenolic liquid, from which we obtained 7 g (27%) of phenol.

4. Decomposition of o-isopropenylphenol by heating. 18.5 g of o-isopropenylphenol, 7.6 g of potassium hydroxide and 4 ml of water were heated in an autoclave at 220° for 3.5 hours. The product was dissolved in water, acidified and the phenolic solution extracted with ether. Distillation yielded 4.1 g of phenol. The residue was a solid, friable resin.

SUMMARY

1. A study was made of the formation and structure of the resin, obtained in the vinylation of phenols.

2. It was established that the resinous products were a mixture containing o-isopropenylphenyl isopropenyl ether and its polymers, obtained by a polymerization of the styrene type.

3. It was shown that the resin obtained by the vinylation of phenols in the presence of potassium hydroxide and water, differed from the alkylphenol – acetylene resins, since it did not contain free hydroxyl groups.

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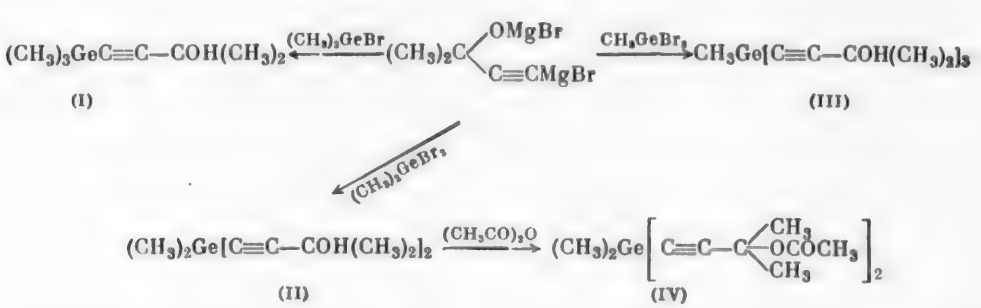
INVESTIGATION IN THE FIELD OF SYNTHESIS AND CONVERSIONS OF UNSATURATED ORGANOGERMANIUM COMPOUNDS

I. SYNTHESIS OF MONO-, DI- AND TRIHYDRIC TERTIARY γ-GERMANIUMACETYLENE ALCOHOLS

I. A. Shikhiev, M. F. Shostakovskii, N. V. Komarov and I. A. Aslanov

The present investigation is a continuation of our work in the field of acetylene alcohols [1], containing germanium in their composition [2].

In previous investigations [1] we studied the interaction of Iotsich's reagent (dimethylethynylmethoxydimagnesium dibromide) with various alkyl(aryl)chlorosilanes. Finally, a method was developed for preparing mono-, di- and trihydric γ-silicon-containing acetylene alcohols. As a further study of the reactions of organoelement compounds with Iotsich's reagent, in the present work we studied the interaction of dimethylethynylmethoxydimagnesium dibromide with methyl-, dimethyl- and trimethylgermanium bromides. During the investigation it was established that the reaction proceeded towards the formation of tertiary γ-germanium-containing acetylene alcohols by the scheme



The presence of a hydroxyl group in the organogermanium acetylene alcohols synthesized was demonstrated by the preparation of the acetate of bis-(2-methylbutyn-3-ol-2)-4-dimethylgermanium (IV). Other reactions of the organogermanium alcohols obtained and their derivatives will be described in subsequent communications.

EXPERIMENTAL

The following starting materials were used: dimethylacetylenylcarbinol with b.p. 102 – 103° (746 mm), n_D^{20} 1.4210, d_4^{20} 0.8580; CH_3GeBr_3 with b.p. 168° (748 mm), n_D^{20} 1.5764, d_4^{20} 2.6325; $(CH_3)_2GeBr_2$ with b.p. 153° (748 mm), n_D^{20} 1.5254, d_4^{20} 2.1170; $(CH_3)_3GeBr$ with b.p. 114 – 115° (748 mm), n_D^{20} 1.4656, d_4^{20} 1.5482.

Synthesis of (2-methylbutyn-3-ol-2)-4-trimethylgermanium (I). With cooling to -10° and stirring, 50 g (0.25 mole) of an ether solution of trimethylgermanium bromide was gradually added to the Iotsich reagent prepared from 0.5 mole of ethylmagnesium bromide and 21 g (0.25 mole) of dimethylethynylcarbinol in the presence of 0.5 g of Cu_2Cl_2 and 1.0 g of $HgCl_2$ [3]. The reaction mixture was heated on a water bath for 8 hours, then treated with 5% hydrochloric acid, neutralized with dilute bicarbonate solution, washed with water and dried with sodium

sulfate. The ether was removed and the residue vacuum distilled. Two distillations yielded 22.6 g (45%) of a substance with b.p. 72 – 73° (7 mm) and m.p. 30°. The product was readily soluble in ether and other organic solvents; it did not give a precipitate with an ammonia solution of silver nitrate.

Found %: C 47.2, 47.32; H 7.96, 8.01; Ge 35.6, 35.9. $C_8H_{16}OGe$. Calculated %: C 47.83; H 8.03; Ge 36.14.

Synthesis of bis-(2-methylbutyn-3-ol-2)-4-dimethylgermanium (II). The synthesis was carried out similarly to the one described above. 24.3 g (1 g-at) of magnesium, 109 g (1 mole) of ethyl bromide, 42 g (0.5 mole) of dimethylethynylcarbinol and 65 g (0.25 mole) of dimethylgermanium dibromide were used. After decomposition of the reaction mixture with 5% hydrochloric acid and appropriate processing, 35.3 g of crystals was obtained and after two recrystallizations from ethanol, these had m.p. 97°. The average yield in a series of experiments was 50 – 53%.

Found %: C 53.9, 53.7; H 7.31, 7.42; Ge 27.5, 27.3. $C_{12}H_{20}O_2Ge$. Calculated %: C 53.60; H 7.50; Ge 27.00.

Synthesis of tri-(2-methylbutyn-3-ol-2)-4-methylgermanium (III). The product was isolated as described above. 14.5 g (0.6 g-at) of magnesium, 65 g (0.6 mole) of ethyl bromide, 27 g (0.32 mole) of dimethylethynylcarbinol and 33 g (0.1 mole) of methylgermanium tribromide were used. We obtained 16.2 g (48%) of a white crystalline substance with m.p. 208°. The product was difficultly soluble in water and ether and readily soluble in alcohol.

Found %: C 57.8, 56.94; H 7.10, 7.16; Ge 21.1, 21.29. $C_{16}H_{24}O_3Ge$. Calculated %: C 57.03; H 7.18; Ge 21.54.

Synthesis of bis-(2-methylbutyn-3-acetoxy-2)-4-dimethylgermanium (IV). 13 g (0.5 mole) of bis-(2-methylbutyn-3-ol-2)-4-dimethylgermanium and 20.4 g (0.2 mole) of acetic anhydride were heated at 80° for 10 hours; two vacuum distillations yielded 10.0 g (57%) of a substance with b.p. 142 – 143° (7 mm) and m.p. 54°.

Found %: C 54.21, 54.16; H 6.62, 6.57; Ge 19.68, 19.82. $C_{16}H_{24}O_4Ge$. Calculated %: C 54.44; H 6.85; Ge 20.69.

SUMMARY

1. The interaction of dimethylethynylmethoxydimagnesium dibromide with alkylgermanium bromides was investigated for the first time and a method was developed for synthesizing a new class of compound, namely, γ-germanium-containing tertiary mono-, di- and trihydric acetylene alcohols.

We obtained and characterized (2-methylbutyn-3-ol-2)-4-trimethylgermanium, bis-(2-methylbutyn-3-ol-2)-4-dimethylgermanium and tri-(2-methylbutyn-3-ol-2)-methylgermanium.

2. A study was made of the interaction of bis-(2-methylbutyn-3-ol-2)-4-dimethylgermanium with acetic anhydride. It was established that this gave the acetate of bis-(2-methylbutyn-3-acetoxy-2)-4-dimethylgermanium.

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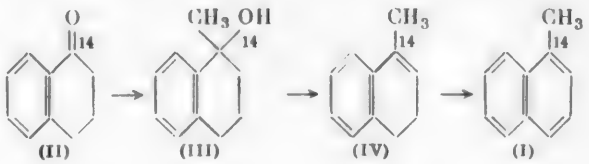
STUDY OF ISOMERIC CONVERSIONS OF ALKYLNAPHTHALENES

II. SYNTHESIS OF 1-METHYLNAPHTHALENE-1-C^{14}

N. N. Vorozhtsov, Jr. and V. A. Koptyug

D. I. Mendeleev Chemico-Technological Institute, Moscow

Up to the present time there have appeared in the literature descriptions of 2-methylnaphthalene-4-C^{14} [1] and 2-methylnaphthalene-8-C^{14} [2], obtained by cyclization of carboxyl-labeled γ-phenyl-β-methylbutyric and γ-(p-tolyl)-butyric acids into the corresponding tetralones with subsequent reduction of the keto group and dehydrogenation of the 2-methyltetrahydronaphthalenes obtained in the presence of palladium. Evidently 1-methylnaphthalenes, labeled in positions 4, 5 and 8 with radiocarbon may be synthesized by an analogous method. However, this method is unsuitable for the synthesis of 1-methylnaphthalene-1-C^{14} (I). We prepared this compound, starting from 1-keto-1, 2, 3, 4-tetrahydronaphthalene-1-C^{14} (II), by the following scheme:



The reaction [3] of 1-keto-1, 2, 3, 4-tetrahydronaphthalene-1-C^{14} [4] with methylmagnesium bromide yielded 1-hydroxy-1-methyl-1, 2, 3, 4-tetrahydronaphthalene-1-C^{14} (III), which was dehydrated into 1-methyl-3, 4-dihydronaphthalene-1-C^{14} (IV) by heating with potassium bisulfate [5] at 120°. Compound (IV) was dehydrogenated to 1-methylnaphthalene-1-C^{14} by heating with sulfur for 15 hours at 220°. When this series of conversions was performed without purification of the intermediate products (III and IV), the yield of 1-methylnaphthalene-1-C^{14} was 78.8%, calculated on 1-keto-1, 2, 3, 4-tetrahydronaphthalene-1-C^{14}.

EXPERIMENTAL

(with the participation of I. S. Isaev and N. A. Morozova)

1-Hydroxy-1-methyl-1, 2, 3, 4-tetrahydronaphthalene-1-C^{14} (III). Into a 250 ml, four-necked flask, fitted with a reflux condenser, a thermometer, a bubbler tube and a stirrer with a mercury seal, were placed 1.66 g (68.3mM) of magnesium turnings and 40 ml of absolute ether and after the stirrer had been switched on, a stream of methyl bromide (~40 ml/min) was passed through the bubbler. The methyl bromide was prepared in a separate apparatus by heating a mixture of 95 ml of methyl alcohol, 40 ml of water, 100 g of concentrated sulfuric acid (d 1.84) and 50 g of potassium bromide • and before entering the reaction flask, it passed through three Drechsel bottles (with concentrated sulfuric acid, water and a 10% solution of sodim hydroxide) and two U-tubes, containing anhydrous calcium chloride. Solution of the magnesium was complete in 30 minutes and then the bubbler was replaced by a dropping funnel and the flask placed in a mixture of ice and salt. The methyl magnesium bromide solution was cooled to -5° and with vigorous stirring, a solution of 8.20 g (56.2 mM) of 1-keto-1, 2, 3, 4, -tetrahydronaphthalene-1-C^{14}•• in 24 ml of absolute ether was added dropwise at such a rate that the temperature

• In mixing the reagents, the potassium bromide was added last.

•• 1-Keto-1, 2, 3, 4-tetrahydronaphthalene-1-C^{14} was prepared from $NaC^{14}N$ with an activity of 23.3 mC/mole

in the flask did not rise above +3°. After the addition, the reaction mixture was stirred for 30 minutes at 0 – +3°, then the cooling bath was removed and stirring continued for a further 8 hours. On the following day, the reaction product was decomposed with 100 ml of a saturated solution of ammonium chloride (the temperature of the mixture was not allowed to rise above +3°) and after the mixture had been stirred for 30 minutes at room temperature, the ether layer was separated. The aqueous layer was extracted with ether. The combined ether extracts were washed with 10% sodium carbonate solution and water and dried with anhydrous sodium sulfate. The dried solution was transferred in portions to a 75 ml flask and the ether removed. The 1-hydroxy-1-methyl-1, 2, 3, 4--tetrahydronaphthalene-1-C^{14}, remaining in the flask as a yellow oil, solidified to a brownish crystalline mass on cooling to room temperature. •

Dehydration of 1-hydroxy-1-methyl-1, 2, 3, 4-tetrahydronaphthalene-1-C^{14} (III). Into the flask containing the unpurified (III) was placed 5.45 g of anhydrous potassium bisulfate and the mixture heated under reflux for 2 hours at a bath temperature of 120°. Water (15 ml) was added to the cooled reaction mixture, which was then extracted with ether. The ether extract was dried with anhydrous sodium sulfate and the ether removed.

1-Methylnaphthalene-1-C^{14}. To the 1-methyl-3, 4-dihydronaphthalene-1-C^{14} (yellow oil) obtained in the previous stage was added 1.78 g (55.6 mg-at) of stick sulfur. The flask was connected to an air condenser with a ground-glass joint, to the top of which was sealed a water condenser, and the mixture heated for 15 hours at a bath temperature of 220°. After being cooled, the reaction mass was shaken with 0.25 g of activated charcoal and 10 ml of ether, filtered, and dried with anhydrous sodium sulfate. The ether was removed, using a Claisen flask, and the 1-methylnaphthalene-1-C^{14} vacuum distilled. The b.p. was 108 – 110° at 12 mm and the yield 6.29 g (78.8%), calculated on the 1-keto-1, 2, 3, 4-tetrahydronaphthalene-1-C^{14}. The product obtained by this procedure was a colorless, mobile liquid with n_D^{20} 1.6159. For highly pure 1-methylnaphthalene, the literature reports b.p. 111° at 12 mm [8] and n_D^{20} 1.61665 [8], 1.6169 [9], 1.6174 [10, 12].

From the 1-methylnaphthalene-1-C^{14} we prepared a picrate with m.p. 138 – 139°, without recrystallization. M.p. 141.5° is reported in the literature [10] for the picrate of 1-methylnaphthalene.

Determination of the radioactivity of the picrate (see [4]) gave the following results.

Found•• %: C 54.9, 55.9. $C_{17}H_{15}O_7N_3$. Calculated %: C 55.0. Radioactivity: 21.1, 21.2 mC/mole.

The 1-methylnaphthalene-1-C^{14} obtained had a refractive index which was slightly lower than that given in the literature for completely pure 1-methylnaphthalene. According to the data of Japanese chemists [9], who dehydrogenated 1-methyl-3, 4-dihydronaphthalene with sulfur at a higher temperature (242 – 245°), this is explained by the presence of sulfur-containing compounds in the product and also by unreacted 1-methyl-3, 4-dihydromethylnaphthalene. However, attempts to detect sulfur compounds in the samples of 1-methylnaphthalene we obtained in model experiments were unsuccessful since a qualitative reaction for sulfur [11] gave negative results; a quantitative determination by a lamp method••• also showed that sulfur was absent from the samples (more accurately, that the content of it was less than 0.1%). The presence of the dihydroderivative in 1-methylnaphthalene was improbable, since it undergoes disproportionation on heating [3]. The most probable impurity was apparently 1-methyl-1, 2, 3, 4-tetrahydronaphthalene and judging by the refractive index, the content of this in the 1-methylnaphthalene-1-C^{14} obtained could not exceed 1.5% (for 1-methyl-1, 2, 3, 4-tetrahydronaphthalene, n_D^{20} 1.5354 is reported in the literature [12]).

In series of model experiments, before vacuum distillation, the 1-methylnaphthalene was purified by conversion into the picrate (m.p. 139 – 140° without recrystallization). 1-Methylnaphthalene isolated from the picrate and distilled had n_D^{20} 1.6172.

SUMMARY

1-Methylnaphthalene-1-C^{14} was synthesized in 78.8% yield, starting from 1-keto-1, 2, 3, 4-tetrahydronaphthalene-1-C^{14}.

• In model experiments, when pressed out on a filter and washed with petroleum ether, the product had m.p. 87.0 – 87.5°, without recrystallization. For 1-hydroxy-1-methyl-1, 2, 3, 4-tetrahydronaphthalene, m.p. 88° [6] and 89° [7] are reported in the literature.

•• Control of the completeness of combustion by the Van Slyke method (see [4]).

••• Possibly a photocolorimetric method - Publisher.

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PREPARATION OF SOME 2, 4-DINITROPHENYL DERIVATIVES OF LYSINE AND THE INTERMEDIATES OF ITS SYNTHESIS

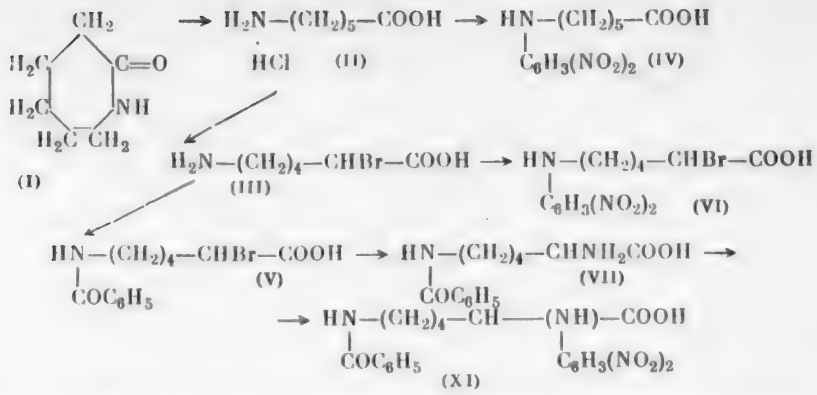
G. A. Garkusha and A. N. Ginsburg

Despite the fact that the dinitrophenylation of amino acids with 2, 4-dinitrochlorobenzene had already been accomplished in 1910 [1], it did not find wide application until 1945, when 2, 4-dinitrofluorobenzene was proposed for this purpose [2]. Up to the present time a considerable number of 2, 4-dinitrophenyl derivatives of amino acids have been synthesized, but for some of them there is contradictory data on their preparation in an individual state. The latter refers particularly to the 2, 4-dinitrophenyl derivative of lysine.

In 1945 Sanger [2] reported that by using 2, 4-dinitrochlorobenzene, he obtained the monohydrochloride of ε-N-2, 4-dinitrophenyllysine with m.p. 186°, and by hydrolysis of α-N-acetyl-ε-N-2, 4-dinitrophenyllysine with 20% HCl. Here it was noted that the author was unable to obtain ε-N-2, 4-dinitrophenyllysine from the complex copper salt of lysine and 2, 4-dinitrochlorobenzene or 2, 4-dinitrofluorobenzene. In 1946, together with the preparation of δ-N-2, 4-dinitrophenylornithine, the author [3] noted the difficulty of isolating both the L-form of ε-N-2, 4-dinitrophenyllysine and its racemate. In 1948 Porter and Sanger [4] reported the preparation of ε-N--2, 4-dinitrophenyllysine, starting from the complex copper salt of lysine and 2, 4-dinitrofluorobenzene, but without giving the melting point or analysis data. In 1953 Carsten and Eisen [5] reported m.p. 182° for ε-N-2, 4-dinitrophenyllysine, quoting m.p. 180°, reported by Porter in his book [6]. The authors [5] obtained and characterized ε-N-2, 4-dinitrophenylaminocaproic acid with m.p. 134°, but gave no data on the yield. In 1954 Rao and Sober [7] characterized the L-form of α-N-ε-N-(bis-2, 4-dinitrophenyl)-lysine with m.p. 170 – 172° (close to m.p. 173 – 174°, reported by Green and Kay [8] and not 146° reported by Porter and Sanger [4] and by Rice and Sowden [9]).

We prepared the ε-N-2, 4-dinitrophenyl (VIII) and ε-N-benzoyl (VII) derivatives of lysine, starting from a solution of the complex copper salt of lysine, protecting the α-amino group in this way. For preparing the complex salt, we did not use basic copper carbonate but a solution of copper nitrate in water and alcohol, from which a solution of the complex copper salt may be prepared at room temperature. The copper was removed from the reaction product by treatment with either HCl (for the benzoyl derivative) or first with HCl and then with H_2S (for the dinitrophenyl derivative). In the latter case, all the deficiencies in the purification of the reaction product, indicated by Porter and Sanger [4], were eliminated. Furthermore, we were able to isolate both the difficultly water-soluble ε-N-2, 4-dinitrophenyllysine with m.p. 193 – 195° (VIII) and its readily soluble monohydrochloride with m.p. 103 – 105° (IX). Analysis data confirmed that this salt did not contain water of crystallization; therefore, m.p. 180, 182 and 186°, reported by Porter and Sanger [4] and also by other authors [5, 6], is explained by insufficient purification of the reaction products.

By benzoylation of the monohydrochloride of ε-N-2, 4-dinitrophenyllysine (IX) by the Schotten-Baumann method, we obtained α-N-benzoyl-ε-N-2, 4-dinitrophenyllysine (X). Its isolation and purification did not present any difficulty, as was the case in the preparation of α-N-2, 4-dinitrophenyl-ε-N-benzoyllysine (XI). We obtained this compound by the dinitrophenylation of ε-N-benzoyllysine (VII), which, in its turn, we obtained both from the complex copper salt of lysine and by synthesis, starting from ε-caprolactam (I) by the following scheme (see formulas I, II, III, V, VII, XI).



It was characterized firstly by the easy and simple preparation of the hydrochloride of ϵ-aminocaproic acid (II) in good yield directly from ϵ-caprolactam; secondly, (II) was directly and simply brominated with red phosphorus and bromine and the yield of ϵ-amino-α-bromocaproic acid (III) was also good. While the dinitrophenylation of ϵ-aminocaproic acid, and likewise the purification of the reaction product, presented no difficulties, the dinitrophenylation of ϵ-amino-α-bromocaproic acid and the isolation of the reaction product in a discrete state required both modification of the reaction conditions and the use of special purification methods.

Since we were unable to carry out the dinitrophenylation of ϵ-amino-α-bromocaproic acid by Sanger's method (with $NaHCO_3$), we accomplished this reaction with Na_2CO_3. Apparently, the presence of a bromine atom in the α-position reduces the basicity of the acid, which affects the pH of the medium. The same occurs in the dinitrophenylation of ϵ-benzoyllysine, where low yields of reaction product are obtained with the use of $NaHCO_3$ and good ones with the use of Na_2CO_3 (here the basicity of ϵ-benzoyllysine is less than that of lysine).

EXPERIMENTAL •

1. ϵ-N-Benzoyllysine (VII). a) Preparation of a solution of the complex copper salt of lysine. To a solution of 5.4 g of lysine monohydrochloride in 17 ml of water was added about 20 ml of N NaOH solution (phenolphthalein gave a light pink color) and the resulting solution was added in portions with stirring to a solution of 3.7 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 15 ml of water; after this, about 9 ml of NaOH solution was added in portions so that the reaction remained acid (to litmus).

b) The benzoylation by the Schotten-Baumann method was carried out at +8° after dilution of solution "a" with water (180 ml) by the alternate addition of 9 ml of benzoyl chloride and about 60 ml of 10% NaOH solution over a period of 3 hours. The acidified reaction mixture was left overnight in a refrigerator and the precipitate separated off, washed with water, pressed out and mixed with ether; the latter was sucked off and the residue washed with ether until the benzoic acid had been removed. The weight of the crystals after recrystallization from boiling water and drying at 100° was 3.5 g. The m.p. was 266°.

Found %: N 10.92. $C_{13}H_8O_3N_2$. Calculated %: N 11.20.

2. Hydrochloride of ϵ-aminocaproic acid (II). 25.0 g of ϵ-caprolactam was boiled for 1 hour with 75 ml of dilute hydrochloric acid [1 volume of HCl (d 1.19) and 3 volumes of water]. The reaction solution was filtered with charcoal and the filtrate evaporated to dryness in vacuum at 60°. The residue was mixed with ether to give a thick mass, which was filtered and washed with ether. The weight of the white lustrous crystals was 34.0 g. After recrystallization from a mixture of alcohol and ether (1 : 1), the product had m.p. 128 – 130°.

Found %: N 8.18. $C_6H_{14}O_2NCl$. Calculated %: N 8.37.

3. ϵ-Amino-α-bromocaproic acid (III). A mixture of 13.5 g of the hydrochloride of ϵ-aminocaproic acid, 3.3 g of powdered red phosphorus and 160 ml of CCl_4 was placed in a three-necked flask, a mechanical stirrer with a mercury seal, a reflux condenser and a dropping funnel; 1/3 of the required volume of bromine (19 ml)

• With the participation of N. A. Ivanchenko

added at +10° over a period of 20 minutes and the other 2/3 at 35 – 40° over 1.5 hours. With continuous stirring, the mixture was heated for a further 2.5 hours at 60 – 65°. The reaction was completed by heating to 80° for 10 minutes. The CCl_4 was removed in vacuum and the viscous reaction product poured into 40 ml of warm water (50°). After being cooled to 0°, the solution was decolorized with Na_2SO_3, filtered with charcoal, and 8% $NaHCO_3$ solution was added (red color with litmus, the color of congo did not change). The filtrate was evaporated in vacuum (50°), and the mineral salts separated and washed with absolute alcohol. After evaporation of the alcohol filtrate, the salts were again separated; if the saturated alcohol solution was turbid, it was again filtered and the solvent removed from it in vacuum (50°). Due to its hygroscopic nature, the solid acid was stored in a vacuum desiccator. The weight was 15.0 g. The m.p. was 102° (uncorr.) and the n_D^{20} 1.386 (50% aqueous solution).

To 3 g of the acid (III) in 30 ml of water were alternately added 6 ml of C_6H_5COCl and about 24 ml of 10% NaOH solution over 3 hours at +10°. The precipitate which separated from the acidified reaction mass was washed with water, treated with ether and then dissolved in alcohol and precipitated with water. After separation, washing with water and drying, its weight was 1.8 g. The m.p. was 161 – 162°.

Found %: N 4.09. $C_{13}H_{16}O_3NBr$. Calculated %: N 4.45.

According to the data in [10], from 1.8 g of ε-benzoylamino-α-bromocaproic acid (V) we obtained ε--N-benzoyllysine (VII) with m.p. 265 – 268°.

4. ε-N-2, 4-Dinitrophenylaminocaproic acid (IV). To a solution of 2 g of the hydrochloride of ε-aminocaproic acid (II) in 80 ml of 50% alcohol was added about 5 ml of 15% Na_2CO_3 solution (a green color with bromothymol) with mechanical stirring. After the addition of a solution of 5.6 g of 2, 4-dinitrofluorobenzene in 72 ml of alcohol and 2.8 g of $NaHCO_3$, a further 1.4 g of $NaHCO_3$ was added in portions. The next day the solution was filtered and about 200 ml of a 20% $BaCl_2$ solution added to it. The yellow precipitate was collected, washed with water, mixed with water acidified with 3% HCl (blue color with congo) and again collected and washed with water. A solution of it in 10% Na_2CO_3 was acidified with 3% HCl and the precipitate collected and washed until chlorine ions were absent. The weight of the crystals (from alcohol) was 1.8 g. The m.p. was 134 – 136° (from alcohol).

Found %: N 13.75; C 48.63; H 5.35. $C_{12}H_{15}O_6N_3$. Calculated %: N 14.01; C 48.48; H 5.05.

5. ε-N-2, 4-Dinitrophenylamino-α-bromocaproic acid (VI). 2.1 g of ε-amino-α-bromocaproic acid (III) with n_D^{20} 1.385 (50% solution in water) in 30 ml of 10% Na_2CO_3 solution (blue color with bromothymol blue) was mixed with 80 ml of 50% alcohol, and a solution of 5.6 g of 2, 4-dinitrofluorobenzene in 72 ml of alcohol added, followed by 2.8 g of Na_2CO_3. After 1/2 hour of mechanical stirring, 1.4 g of Na_2CO_3 was added in portions over a period of 2 hours (the reaction mixture had to be alkaline to bromothymol blue). On the next day, the filtrate was treated with chloroform in a separatory funnel. The aqueous layer was acidified with 3% HCl and the yellow, viscid mass was washed with water by decantation, dissolved in 10% Na_2CO_3 solution, filtered with charcoal and 30 ml of 20% $CaCl_2$ solution added. The yellow precipitate was collected, washed and mixed with water and after acidification with 3% HCl, the viscid mass dissolved in sodium carbonate as was done the first time. Finally, the viscid mass, weighing 1.3 g, was recrystallized from hot 50% alconol 3 – 4 times. The m.p. was 160 – 165° (with decomp.) and the n_D^{20} 1.388 (solution of 1 part of acid in 4 parts of N NaOH solution).

Found %: N 11.08. $C_{12}H_{14}O_6N_3Br$. Calculated %: N 11.15.

6. ε-N-2, 4-Dinitrophenyllysine (VIII). To a solution of the complex copper salt of lysine, prepared from 1.3 g of $Cu(NO_3)_2 \cdot 3H_2O$ with 5 ml of water, 1.5 g of lysine monohydrochloride in 5 ml of water and 9.5 ml of 1 N NaOH solution and diluted with 80 ml of 50% alcohol, was added a solution of 4.5 g of 2, 4-dinitrofluorobenzene in 60 ml of alcohol, followed by 2.5 g of $NaHCO_3$ in portions over a period of 2 hours with mechanical stirring. The next day the precipitate was separated, washed with water and ether, stirred with 8 ml of HCl(1 : 2) (avoiding an excess) until it dissolved, then evaporated to a thick mass in vacuum and the precipitate separated and washed with ether until the drops were colorless. The yellow precipitate was dissolved in 4 – 5 times its volume of water with acidification with HCl (1 : 2) (blue color with congo) and the CuS precipitated with hydrogen sulfide. The CuS was removed and the yellow precipitate obtained from the filtrate (by evaporation in vacuum at 40°) dissolved in 1 N HCl. The filtered solution was neutralized with $NaHCO_3$ and the precipitate separated and washed with water. The weight was 1.0 g. The m.p. was 193 – 195°.

Found %: N 16.47; C 45.96; H 5.38. $C_{14}H_{16}O_6N_4$. Calculated %: N 16.66; C 46.72; H 5.12.

The hydrochloride of ε-N-2, 4-dinitrophenyllysine (IX) was obtained from 1.0 g of the acid by solution in 3% HCl. The filtrate was evaporated in a vacuum desiccator. The residue was collected, washed with ether and recrystallized from anhydrous alcohol. The weight was 0.6 g. The m.p. was 103 – 105°.

Found %: N 16.25; C 41.69; H 5.36. $C_{12}H_{17}O_6N_4Cl$. Calculated %: N 16.00; C 41.88; H 4.87.

7. ε-N-2, 4-Dinitrophenyl-α-N-benzoyllysine (X). At +10° and with mechanical stirring, 3.15 ml of C_6H_5COCl and 35 ml of 10% NaOH solution were added alternately (by the Schotten-Baumann method) over a period of 2 hours to a solution of 2.5 g of the hydrochloride of ε-N-2, 4-dinitrophenyllysine (IX) in 100 ml of water. The next day, the yellow precipitate, obtained after acidification of the reaction mixture with HCl, was collected, washed with water and treated with ether to remove benzoic acid. The weight was 2.2 g. The product was recrystallized by solution in hot alcohol and precipitation with water. The m.p. was 167 – 169° (uncorr.).

Found %: N 13.22; C 55.00; H 5.00. $C_{19}H_{20}O_7N_4$. Calculated %: N 13.46; C 54.80; H 4.80.

8. ε-N-Benzoyl-α-N-2, 4-dinitrophenyllysine (XI). A solution of 4.5 g of 2, 4-dinitrofluorobenzene in 50 ml of alcohol was added dropwise with mechanical stirring to a solution of 2.0 g of ε-N-benzoyllysine (VII) in 600 ml of water, acidified with 2.8 ml of dilute HCl (1 : 1).

2.8 g of Na_2CO_3 was added in portions over a period of 3 hours and 2.2 g of Na_2CO_3 over 1 hour (blue color with bromothymol blue). The next day the reaction mixture was acidified with HCl (1 : 1) (blue color with congo) and the viscous yellow mass separated by decantation and washed with water and ether by the same method. The mass was dissolved in hot alcohol and precipitated with water. The weight was 1.5 g. The precipitate was recrystallized from alcohol and water. The m.p. was 182 – 185°.

Found • %: N 13.76; C 54.43; H 5.00. $C_{19}H_{20}O_7N_4$. Calculated %: N 13.46; C 54.80; H 4.80.

SUMMARY

1. ε-N-2, 4-Dinitrophenyl-α-bromocaproic acid and ε-N-2, 4-dinitrophenyl-α-N-benzoyllysine, which are not described in the literature, were prepared.

2. A method was described for preparing ε-N-2, 4-dinitrophenyllysine and ε-N-2, 4-dinitrophenylcaproic acid.

3. A scheme was put forward for the synthesis of ε-amino-α-bromocaproic acid, starting from ε-caprolactam.

4. A method was put forward for the preparation of α-N-benzoyllysine, starting from lysine, $Cu(NO_3)_2 \cdot 3H_2O$ and C_6H_5COCl.

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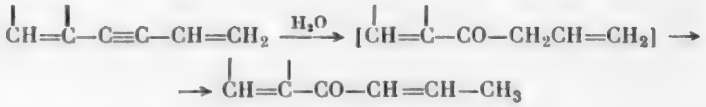
• The microanalyses of the substances were carried out by V. D. Zolotnikova.

INVESTIGATION OF THE STRUCTURE OF THE PRODUCTS OF HYDRATION OF DI- Δ^1-CYCLOHEXENYLACETYLENE

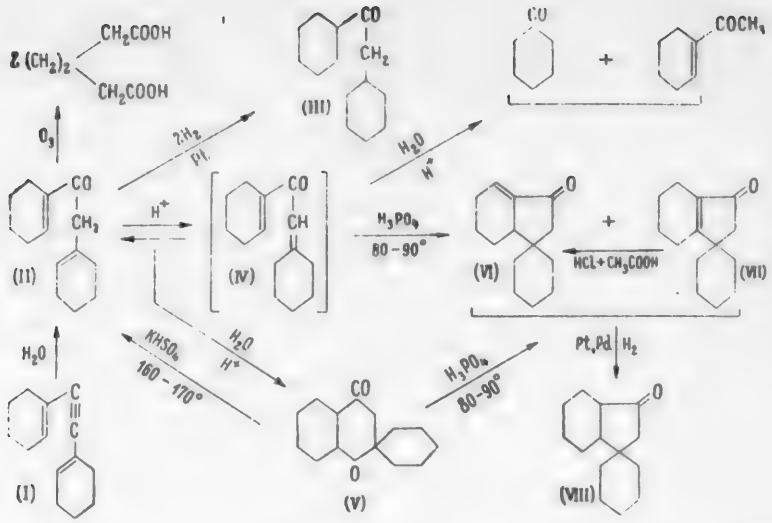
I. N. Nazarov and I. I. Zaretskaya

Institute of Organic Chemistry of the Academy of Sciences of the USSR

In the preceding communication it was shown that hydration of a number of divinylacetylenic hydrocarbons in aqueous methanol in presence of mercury salts yielded not only the expected vinyl allyl ketones but also the isomeric vinyl propenyl ketones [1].



These results are in line with numerous publications which indicates the facility of migration of an isolated β, γ-double bond into a conjugate α, β-position under the influence of acid and alkaline reagents [2]. The α, β-position of a double bond is not, however, in all cases the most stable position. Linstead and co-workers showed that the β, γ-form is the most stable in ketones and acids with an iso structure [3]. An equilibrium between the α, β- and β, γ-isomers is established in compounds with cyclic radicals under the influence of isomerizing agents, and in a number of cases the β, γ-form predominates [4]. These facts prompted us to use di- Δ^1-cyclohexenylacetylene (I) for the synthesis of a dienone with a stable β, γ-double bond (vinyl allyl ketone). Hydration of this dienyne was previously effected in our laboratory but the structure of the resulting product was not investigated [5]. Heating of dienyne (I) in 90% methanol in presence of mercuric sulfate gave 1, 2-di-(Δ^1-cyclohexenyl)-ethanone (II) in 82% yield; its structure was confirmed by hydrogenation and ozonization and by the ultraviolet absorption spectrum. The dienone (II) absorbs 2 moles hydrogen on hydrogenation in ethanol with platinum oxide and gives cyclohexylhexahydrobenzyl ketone, which has been described in the literature (III) [6]. Ozonization of dienone (II) in chloroform gave 55% of adipic acid (calculated on 2 moles). Cyclohexanone could not be detected at all in the products of ozonization, although it might have been formed in presence of the isomeric 1-Δ^1-cyclohexenyl-2-cyclohexylidene-ethanone (IV). The maxima of the absorption spectra of dienone (II) itself (λ_{max} in alcohol 237 mμ) and of its semicarbazone (λ_{max} in alcohol 260 mμ) were likewise found to be characteristic of ketones with one conjugated double bond. Consequently the β, γ-double bond in the six-membered ring was also stable, as had been expected, and did not migrate to the conjugate α, β-position even under hydration conditions, as had occurred in the aliphatic series [1]. Our attempts to isomerize dienone (II) to dienone (IV) and to isolate the latter in the pure form were unsuccessful. Treatment with sodium ethoxide in ethanol at room temperature gave a product with a too-low percentage of carbon and a lower refractive index. Isomerization in presence of hydrochloric acid in ethanol at room temperature led to recovery of some unchanged dienone together with the product of its hydration, 2, 2-pentamethylenehexahydro-4-chromanone (V). However, the ultraviolet absorption maximum of the 2, 4-dinitrophenylhydrazone (λ_{max} in isooctane 369 mμ), prepared from dienone (II), indicates that such an isomerization does occur in an acid medium. Migration of an isolated β, γ-double bond into the conjugated α, β-position under conditions of preparation of 2, 4-dinitrophenylhydrazones has been described in the literature [7]. Formation of the unstable intermediate dienone (IV) is also confirmed by the reactions (see below) of cyclization, hydration and hydrolytic cleavage.

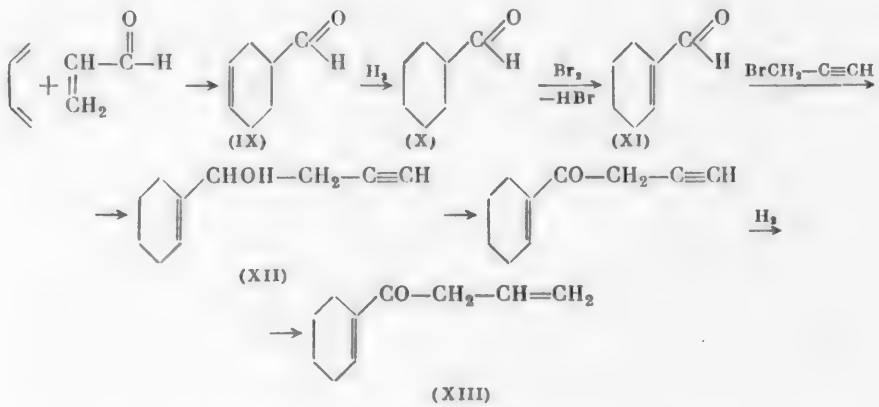


As we mentioned above, the dienone (II) easily hydrolyzes in an acid medium at room temperature with formation of chromanone (V). The latter is also obtained in considerable quantity on hydrolysis of the semicarbazone and 2, 4-dinitrophenylhydrazone obtained from dienone (II). Unless precautionary measures are taken, the dienone obtained on hydration of dienone (II) is always contaminated by chromanone (V); it could not be freed of the latter by the usual fractional distillation. Chromanone (V) was obtained in 60% yield when dienone (II) was boiled with hydrochloric acid in isopropyl alcohol. It is isolated in the form of snow-white, well-formed crystals and readily forms a semicarbazone and a 2, 4-dinitrophenylhydrazone. The absence of an active hydrogen in the chromanone (V) and the absorption maximum of 1715 cm^{-1} in the ultraviolet indicate that ring-closure occurred with formation of a six-membered pyran ring, and not of a five-membered ring as we had previously found in the case of 5-methyl-1, 5-heptadien-4-one [9]. Treatment of dienone (II) with hydrochloric acid as well as with potassium bisulfate at 165 – 170° gave small quantitites of cyclohexanone and methylcyclohexenyl ketone. The latter could have been formed by hydrolytic cleavage of the double bond in the seven-membered ring, and this would afford additional proof of the ability of dienone (II) to isomerize to dienone (IV) under the influence of acid reagents. A number of studies by M. M. Shemyakin and his co-workers [10] have been devoted to the hydrolytic cleavage of α, β-unsaturated ketones under the influence of acid and alkaline agents. Stirring of chromanone (V) with phosphoric acid (d 1.7) at 80 – 90° for 2 hours leads to a mixture of isomeric crystalline spiroindanones (VI) and (VII). The ratio of these isomers depends on the reaction conditions, but the low-melting isomer (VI) always predominates. Formation of spiroindanones (VI) and (VII) from chromanone (V) presupposes initial cleavage by the Petrenko-Kritchenko mechanism [11] with formation of the intermediate dienone (IV) which then cyclizes. Heating of chromanone (V) with potassium bisulfate gave dienone (III) in high yield and insignificant quantities of cyclohexanone and methylcyclohexenyl ketone. In this case spiroindanones (VI) and (VII) were not detected at all.

It should be noted that, unlike dienones of the aliphatic series or those with one cyclic substitutent, dienone (II) requires drastic conditions for cyclization. Prolonged contact with acids at room temperature leads to formation of a considerable quantity of chromanone (V). Heating with phosphoric acid at 80 – 90° but without stirring also gives a mixture of the original dienone and chromanone (V). We isolated a mixture of spiroindanones (VI) and (VII) in 3:1 ratio only after stirring dienone (II) with phosphoric acid (d 1.7) at 80 – 90° for 3 hours. We previously described suppression of cyclization due to hydration of the α, β-double bond, with formation of derivatives of tetrahydro-γ-pyrone, in connection with the behavior of vinyl propenyl ketone [8]. Cyclohydration of dienyne (I) scarcely takes place with acids – phosphoric, concentrated hydrochloric, and formic – under conditions milder than those described by Marvel [12]. The cyclic ketones (VI) and (VII) isolated from the chromanone (V), and also obtained on cyclization of dienone (II), had constants perfectly identical with those of the ketones obtained by Linstead and his co-workers by cyclohydration of dienyne (I) [13]. At first the authors assigned to these ketones the structure of dodecahydrophenanthrone, but this was later refuted [14]. On the basis of ultraviolet spectrographic

data, Woodward [15] concluded that the double bond in ketone (VI) is in the 4 – 9 position (exocyclic), and that in ketone (VII) in the 8 – 9 position (endocyclic) [15]. We repeated Linstead's experiments on the hydrogenation of these ketones and investigated their isomerization. Ketones (VI) and (VII) absorb more than one molecule of hydrogen during hydrogenation in presence of platinum oxide and palladium-on-carbon, and give mainly 1, 1--spirocyclohexane-hydroindanone-3 (VIII). Ketone (VII) is hydrogenated more rapidly than (VI). When ketone (VII) is boiled with a mixture of hydrochloric and acetic acids in xylene, it nearly entirely isomerizes to (VI). We observed a similar isomerization under hydrogenation conditions. We isolated a substance isomeric with the saturated ketone (VIII), via the 2, 4-dinitrophenylhydrazone, from the products of hydrogenation of ketones (VI) and (VII). This compound is probably a stereoisomer. According to Linstead the latter cannot be isomerized to (VIII).

We attempted to effect a synthesis of vinyl allyl ketones, as exemplified by allyl-Δ^1-cyclohexenyl ketone (XIII) – by the following scheme:



Treatment of Δ^1-tetrahydrobenzaldehyde with propargyl bromide in presence of zinc amalgam in solution in a mixture of tetrahydro-2-methylfuran and ether gave 1-Δ^1-cyclohexyl-3-butyn-1-ol (XII) in 60 – 65% yield; numerous attempts were made to oxidize this compound with manganese dioxide, chromic oxide in acetic acid and sulfuric acid, and potassium dichromate in 2 N sulfuric acid, but without success. Nearly the whole of the original carbinol was recovered. We had previously obtained similar results in attempts to oxidize allyl-Δ^1-cyclohexenylcarbinol [1].

EXPERIMENTAL

Dicyclohexylol-acetylene with m p. 107 – 108° was prepared by the method previously described [5].

Dehydration of dicyclohexylol-acetylene. A mixture of 100 g diol and 100 g 40% sulfuric acid was stirred 3 hours at 95 – 100°. The upper layer was collected and the lower layer extracted with ether. The combined solution was neutralized with sodium carbonate and dried over sodium sulfate. Fractional distillation gave 70 g (83%) di-Δ^1-cyclohexenylacetylene (I), b.p. 126 – 128° (3 mm), n_D^{20} 1.5585 [12]. From the residue was isolated a further 10 g dienyne contaiminated with a higher boiling product with b.p. 130 – 140° (3 mm), n_D^{20} 1.5530.

Hydration of di-Δ^1-cyclohexenylacetylene (I). A mixture of 19 g dienyne, 80 ml 90% methanol and 1 g mercuric acetate was stirred 1.5 hour at 65 – 70°. Another 2 g catalyst was introduced in portions in the course of the reaction. Stirring was continued at this temperature for a total of 5.5 hour. The methanol was distilled off in a low vacuum. The residue was diluted with water, neutralized with sodium carbonate, extracted with ether and dried over sodium sulfate. Fractionation gave 17 g (82%) of 1, 2-di-(Δ^1-cyclohexenyl)-ethanone (II):

B.p. 124 – 125° at 2 mm, 133 – 134° at 3 mm, 149 – 150° at 6 mm; n_D^{20} 1.5330, d_4^{20} 1.0134, MR_D 62.6; Calc. 61.53; λ_{max} (in methanol) 237 mμ; ϵ_{max} 3.91.

Found %: C 82.33, 82.13; H 9.92, 9.93. $C_{14}H_{20}O$. Calculated %: C 82.35; H 9.86.

Semicarbazone, m.p. 172 – 173° (from methanol); λ_{max} (in ethanol) 260 mμ.

2, 4-Dinitrophenylhydrazone in the form of dark-orange crystals, m.p. 130 – 131° (from ethanol + ethyl acetate); λ_{max} (in isopentane) 369 mμ.

Found %: C 62.28, 62.27; H 6.27, 6.29; N 14.63, 14.73. $C_{20}H_{24}O_4N_4$. Calculated %: C 62.48; H 6.29; N 14.57.

A small quantity of the 2, 4-dinitrophenylhydrazone of the chromanone (V) was isolated from the mother liquor; m.p. 203 – 205°.

Hydrogenation of 1, 2-di-(Δ^1-cyclohexenyl)-ethanone (II). 3 g dienone in 6 ml ethanol was hydrogenated in presence of platinum oxide. In 2 hours 662 ml hydrogen was taken up (theoretical requirement for 2 double bonds 666 ml). Fractionation gave 2 g cyclohexylhexahydrobenzyl ketone (III), b.p. 135 – 137° (6 mm), n_D^{20} 1.4840.

Semicarbazone, m.p. 186 – 187° (from methanol); 2, 4-dinitrophenylhydrazone in the form of straw-yellow needles, m.p. 131 – 132° (from ethanol); λ_{max} (in isopentane) 345 mμ.

Ozonization of 1, 2-di-(Δ^1-cyclohexenyl)-ethanone (II). Ozonized oxygen (6% ozone) was passed into a solution of 3.65 g dienone (b.p. 137 – 139° at 4 mm, n_D^{20} 1.5335) in 40 ml dry chloroform at a rate of 6-6.5 ml./ /hr for 7.5 hr. The ozonide (in the form of a yellow gel) was stirred for 1/2 hour with water (50 ml) at 60 – 70°; 10 ml 8% hydrogen peroxide was then added, and stirring was continued at the same temperature for another 2 hours. The products of oxonolysis were neutralized with sodium carbonate (3.8 g) and the neutral products of extraction were extracted with ether. The ether was driven off and from the residue (1 g) was distilled 0.3 g of a substance (b.p. 100 – 110° at 6 mm, n_D^{20} 1.4820) from which was isolated the 2, 4-dinitrophenylhydrazone of chromanone (V), m.p. 200 – 203°. A mixture with the specimen described above did not exhibit a depression of melting point. The water was driven off from the salts of the acids and the residue was decomposed with 15 ml concentrated hydrochloric acid. The organic acids were extracted with ether. Recrystallization from concentrated acid gave 2 g adipic acid with m.p. 150 – 151°. No depression of melting point in a mixed melting test with an authentic specimen was found.

Hydrolysis of the 2, 4-dinitrophenylhydrazone of dienone (II). 5 g of the compound (m.p. 130 – 131°), 10 ml pyruvic acid, 11.5 g sodium acetate, 250 ml water and 325 ml acetic acid were stirred 4 hours at 110 – 120°. The main bulk of the acetic acid was taken off in vacuum. The residue was neutralized with sodium carbonate and extracted with ether. The precipitate of the 2, 4-dinitrophenylhydrazone of pyruvic acid was washed with ether. The ether was driven off and the residue was fractionated to give a 2 g substance (b.p. 149 – 150° at 6 mm, n_D^{20} 1.5225, d_4^{20} 1.0214) from which were obtained the 2, 4-dinitrophenylhydrazones of dienone (II) with m.p. 130 – 131° and of chromanone (V) with m.p. 205 – 206°.

Hydrolysis of the semicarbazone of dienone (II). 2.2 g semicarbazone (m.p. 172 – 173°) in 10 ml benzene and 10 ml 10% sulfuric acid were stirred 9 hours at 70°. Part of the semicarbazone (70 mg) was not hydrolyzed. The solution was extracted with ether. After the ether had been driven off, the residue was fractionally distilled. A substance (1 g) was obtained with b.p. 125 – 127° at 2 mm, n_D^{20} 1.5240, from which were obtained the 2, 4-dinitrophenylhydrazone (m.p. 130 – 131°) and semicarbazone (m.p. 172 – 173°) of the original dienone (II), as well as the 2, 4-dinitrophenylhydrazone (m.p. 205 – 206°) and the semicarbazone (m.p. 227 – 228°) of chromanone (V) in the approximate ratio of 1:1.

Attempts to isomerize 1, 2-di-(Δ^1-cyclohexenyl)-ethanone (II). A. With hydrochloric acid. 1) A solution of 1.9 g dienone (b.p. 133 – 134° at 3 mm, n_D^{20} 1.5320) in 40 ml ethanol (95%) and 20 ml concentrated hydrochloric acid was left 18 hours at 20°. The ethanol was taken off by heating in a low vacuum, and the residue was fractionated to give 1.5 g of a substance with b.p. 140 – 142° at 5 mm, n_D^{20} 1.5250, from which were separated the 2, 4-dinitrophenylhydrazones of the original dienone (II) (m.p. 130 – 131°) and of the chromanone (V) (m.p. 205 – 206°).

2) A solution of 10 g dienone (b.p. 128 – 130° at 2 mm, n_D^{21} 1.5330), 80 ml isopropyl alcohol and 3 ml concentrated hydrochloric acid was left 21 hours at 18 – 20°. The product was diluted with water, neutralized with sodium carbonate, extracted with ether and dried with sodium sulfate. There was obtained 8.2 g dienone (II) (b.p. 139 – 140° at 4 mm, n_D^{20} 1.5310). Ozonization of 5 g of this product gave 4 g adipic acid with m.p. 149 – 150° and 0.75 g of a neutral substance (n_D^{20} 1.4875) whose 2, 4-dinitrophenylhydrazone melted at 200 – 203° and did not give a depression in a mixed melting test with the 2, 4-dinitrophenylhydrazone of chromanone (V). Cyclohexanone was not detected in the neutral products.

3) Treatment of 3 g dienone (II) (n_D^{20} 1.5340) in 15 ml isopropyl alcohol with 3 ml concentrated hydrochloric acid for 90 hours at 18 – 20° likewise gave 2.5 g of a mixture of the original dienone (II) and chromanone (V) (b.p. 136 – 138° at 4 mm, n_D^{20} 1.5250). A mixture of the 2, 4-dinitrophenylhydrazones with the specimens described above did not exhibit a depression.

B) With sodium ethoxide. A solution of 4 g dienone (II) (b.p. 137 – 140° at 4 mm, n_D^{20} 1.5320) and 200 ml 2% sodium ethoxide (C_2H_5OH – 95%) was left 18 hours at 18 – 20°; the product was diluted with water and extracted with ether. The ethereal solution was washed with acetic acid. Fractional distillation gave 3 g of a substance with b.p. 135 – 137° at 3 mm, n_D^{20} 1.5225.

Found %: C 79.80, 80.37; H 9.97, 10.04. $C_{14}H_{20}O$. Calculated %: C 82.35; H 9.86.

The 2, 4-dinitrophenylhydrazone, m.p. 130 – 131°, does not give a depression with the 2, 4-dinitrophenylhydrazone obtained from dienone (II).

Treatment of 3 g dienone (II) at 15 – 20° with sodium ethoxide (2 g Na in 50 ml anhydrous alcohol) for 90 hours gave 2 g of a substance with b.p. 142 – 145° at 5mm, n_D^{19} 1.5235. The 2, 4-dinitrophenylhydrazone (m.p. 128 – 129°) does not exhibit a depression of melting point in admixture with the above-described specimen.

C) With mercuric sulfate. A solution of 6.6 g dienone (II) (b.p. 141 – 142° at 4 mm, n_D^{20} 1.5320) in 20 ml anhydrous benzene and 1.1 g mercuric sulfate were stirred at boiling for 5 hours. The mass was worked up to give 5.6 g of the original dienone; n_D^{17} 1.5350.

Preparation of 2, 2-pentamethylene-hexahydrochromanone-4 (V). A solution of 17.6 g dienone (II) (b.p. 139 – 140° at 4 mm, n_D^{20} 1.5330) in 55 ml isopropyl alcohol and 10 ml concentrated hydrochloric acid was stirred at boiling for 2 hours. The solvent was taken off in vacuum and the residue was recrystallized from ethanol. There was obtained 8 g (V) in the form of snow-white crystals with m.p. 68 – 69°. Infrared spectrum: 1715 cm^{-1}; ultraviolet spectrum: λ_{max} 285 mμ (ethanol), ϵ_{max} 1.522. It does not decolorize a solution of bromine in chloroform and gives a negative reaction for active hydrogen in the Tserevitinov test.

Found %: C 75.86, 75.77; H 10.06, 10.19. $C_{14}H_{22}O_2$. Calculated %: C 75.67; H 9.98.

The 2, 4-dinitrophenylhydrazone formed golden crystals (from ethanol and ethyl acetate), m.p. 205 – 206°; λ_{max} (in isooctane) 349 mμ. It does not give a depression of melting point with the above-described specimens.

Found %: C 59.95, 59.87; H 6.50, 6.46; N 14.18, 14.15. $C_{20}H_{26}O_5N_4$. Calculated %: C 59.72; H 6.46; N 13.92.

Semicarbazone, m.p. 227 – 228° (from alcohol).

Fractional distillation of the mother liquor after the crystals had been frozen out yielded 8.1 g of a substance with b.p. 139 – 140° at 4 mm, n_D^{20} 1.5270, from which, by two treatments with concentrated hydrochloric acid as indicated above, was isolated another 2 g of chromanone (V) with m.p. 64 – 65°. Total yield of chromanone, 10 g, is 57% calculated on the dienone taken. In addition the mother liquor yielded 0.5 g of substance with b.p. 70 – 80° at 4 mm, n_D^{20} 1.4800 in which were identified (through the 2, 4-dinitrophenylhydrazones) cyclohexanone with m.p. 157 – 160° (no depression with an authentic specimen), and methyl cyclohexenyl ketone with m.p. 202 – 203°; λ_{max} (isooctane) 363 mμ. No depression of melting point in admixture with an authentic specimen was seen.

Found %: C 55.18, 55.40; H 5.22, 5.37. $C_{14}H_{16}O_4N_4$. Calculated %: C 55.26; H 5.30.

According to the literature methyl cyclohexenyl ketone has the following constants: b.p. 96 – 98° at 22 mm, n_D^{16} 1.4872; 2, 4-dinitrophenylhydrazone: m.p. 199 – 201° [18].

Decomposition of the semicarbazone of chromanone (V). a) 2.7 g semicarbazone (m.p. 227 – 228°) in 30 ml benzene was stirred 12 hours with 12 ml 10% sulfuric acid at 75 – 85°. There was isolated 0.7 g of the original semicarbazone and 1 g chromanone (V) with m.p. 68 – 69°.

b) To 0.3 g semicarbazone (m.p. 227 – 228°) was added 3 ml concentrated hydrochloric acid at room temperature. 9 ml water was added to the filtered solution. There was isolated 150 mg (65%) of chromanone (V) with m.p. 64 – 65°.

Cleavage of 2, 2-pentamethylene-hexahydrochromanone-4 (V) by potassium-bisulfate. A mixture of 2 g chromanone (m.p. 68 – 69°) and 1 g calcined potassium bisulfate was heated 1 hour at 155 – 160°. Fractional distillation gave 1.4 g 1, 2-di-(Δ^1-cyclohexenyl)-ethanone (II) with b.p. 140 – 141° at 4 mm; n_D^{20} 1.5315; 2, 4-dinitrophenylhydrazone, m.p. 130 – 131°. A mixed melting test with the above-described specimens did not give a depression. From the first drops (n_D^{20} 1.4670) were isolated the 2, 4-dinitrophenylhydrazones of cyclohexenone (m.p. 159 – 160°) and of methyl cylohexenyl ketone (m.p. 201 – 203°). A mixed melting test with authentic specimens did not give a depression.

Hydrolytic cleavage of 1, 2-di-(Δ^1-cyclohexenyl)-ethanone (II). A mixture of 11 g dienone (b.p. 129 – 130° at 2.5 mm, n_D^{21} 1.5310), 5 g potassium bisulfate and a few drops of water was heated 2 hours at 160 – 170°. Fractional distillation yielded 8.7 g of the original dienone with b.p. 149 – 150° at 6 mm (n_D^{20} 1.5330) and 0.6 g of cleavage products (b.p. 70 – 80° at 7 mm, n_D^{20} 1.4850). In this mixture were identified (via their 2, 4-dinitrophenylhydrazones) cyclohexanone (m.p. 159 – 160°) and methyl cyclohexenyl ketone (m.p. 202 – 203°). No depression in admixture with authentic specimens was found.

Cleavage of 2, 2-pentamethylene-hexahydrochromanone-4 (V) by phosphoric acid. a) A mixture of 5 g chromanone (m.p. 68 – 69°) and 12 g phosphoric acid (d 1.7) was stirred 3 hours at 80 – 85°. The product was diluted with water, neutralized with sodium carbonate and extracted with ether. The ethereal solution was dried over sodium sulfate. After the ether had been driven off, the residue crystallized. There was obtained 0.65 g 1, 1-spirocyclohexane-$\Delta^{8(9)}$-tetrahydro-3-indanone (VII) with m.p. 93 – 94° (from 50% ethanol).

2, 4-Dinitrophenylhydrazone, m.p. 186 – 187°; λ_{max} (isooctane) 371 mμ. Semicarbazone, m.p. 231 – 232°.

Fractional distillation of the mother liquor yielded 2.5 g of substance with b.p. 140 – 141° at 3 mm, n_D^{20} 1.5370, from which was obtained the 2, 4-dinitrophenylhydrazone of 1, 1-spirocyclohexane-$\Delta^{4(9)}$-tetrahydroindanone-3 (VI) in nearly quantitative yield; m.p. 226 – 227°; λ_{max} (isopentane) 378 mμ. Semicarbazone, m.p. 226 – 227°.

b) A mixture of 8.8 g chromanone (V) (m.p. 68 – 69°) and 25 ml phosphoric acid (d 1.7) was stirred 2 hours at 80 – 85°. The mass was worked up as described above and yielded 1 g ketone (VII) with m.p. 92 – 93° and 5 g substance with b.p. 144 – 146° at 4 mm, n_D^{20} 1.5375; freezing of the latter in dry ice yielded 2.3 g crystals with m.p. 28 – 30°. Recrystallization from ligroine gave 1.3 g ketone (VI) with m.p. 34 – 35°.

The ketones isolated by Linstead after cyclohydration of dienyne (I) had the following constants: (VI) m.p. 39°; λ_{max} (in ethanol) 241 mμ; ϵ_{max} 3.95; 2, 4-dinitrophenylhydrazone, m.p. 227 – 228°; semicarbazone, m.p. 227 – 228°; (VII) m.p. 94°; λ_{max} (in ethanol) 247 mμ; ϵ_{max} 4.09. 2, 4-Dinitrophenylhydrazone, m.p. 186 – 187°; semicarbazone, m.p. 231 – 232°.

Isomerization of 1, 1-spirocyclohexane-$\Delta^{8(9)}$-tetrahydro-3-indanone (VII). a) A solution of 100 mg ketone (m.p. 93 – 94°), 3 ml xylene, 3 ml glacial acetic acid and 4 ml concentrated hydrochloric acid was stirred 8 hours at 125 → 130°. The upper layer was washed with sodium carbonate solution and water. The solvent was driven off and the residue distilled. The latter gave the 2, 4-dinitrophenylhydrazone of the isomeric cyclic ketone (VI) with m.p. 225 – 226° in 70% yield. (Isomerization was also effected in toluene solution at 110 – 115°.)

b) A mixture of cyclic ketones (VI) and (VII) (10 g), obtained by cyclohydration of dienyne (I) with formic acid (b.p. 131 – 137° at 3 mm, n_D^{20} 1.5370), was heated 3 hours with 12 g phosphoric acid (d 1.7) at 170 – 180°. After working-up and fractional distillation, there was obtained 5 g ketone (VI), m.p. 28 – 30° (b.p. 150 – 152° at 5 mm, n_D^{20} 1.5370); 2, 4-dinitrophenylhydrazone, m.p. 224 – 225°. There was no depression in admixture with with the 2,4-dinitrophenylhydrazone of ketone (VI)

Hydrogenation of 1, 1-spirocyclohexane-$\Delta^{8(9)}$-tetrahydro-3-indanone (VII). Hydrogen was passed into a solution of 934 mg ketone (m.p. 93 – 94°) in 20 ml ethanol in presence of platinum oxide and palladium-on-carbon. After 15 min 150 ml of hydrogen had been taken up (requirement for one double bond-105 ml). The following were identified in the residue, after removal of the solvent, via the 2, 4-dinitrophenylhydrazones: 1) 1, 1-spirocyclohexane-hexahydro-3-indanone (VIII), m.p. 160 – 161° in the form of yellow needles (from ethanol - ethyl acetate); λ_{max} (in isooctane) 345 mμ.

Found %: C 62.10, 62.25; H 6.88, 6.89. $C_{20}H_{26}O_4N_4$. Calculated %: C 62.20; H 6.78.

2) 1, 1-Spirocyclohexane-$\Delta^{4(9)}$-tetrahydroindanone (VI) with m.p. 224 – 225°; 3) A substance with m.p. 185 – 186° in the form of dark-orange needles; λ_{max} (in isooctane) 348 mμ. It gives a depression with the 2, 4-dinitrophenylhydrazone of the original ketone (VI).

Found %: C 62.56; H 6.76. $C_{20}H_{26}O_4N_4$. Calculated %: C 62.20; H 6.78.

Hydrogenation of 1, 1-spirocyclohexane-$\Delta^{4(9)}$-tetrahydro-3-indanone (VI). Hydrogen was passed into a solution of 977 mg ketone (m.p. 34 – 35°) in 20 ml ethanol in presence of platinum oxide and palladium-on-carbon. Hydrogenation went very slowly. After 7 hours 185 ml hydrogen had been absorbed (the theoretical requirement is 106 ml). After removal of the solvent, the residue was found (via the 2, 4-dinitrophenylhydrazones) to contain ketone (VII) with m.p. 160 – 161° and an isomeric ketone of unknown structure with m.p. 186 – 187°. A mixture with the above-described specimens did not give a depression.

Cyclohydration of 1, 2-Δ^1-cyclohexenylacetylene. (I). a) A mixture of 5.4 g dienyne (b.p. 131 – 133° at 4 mm, n_D^{19} 1.5585) and 5 g phosphoric acid (d 1.7) was heated 5 hours at 70°. Fractional distillation yielded 4.5 g of the original dienyne and traces of dienone (II).

b) A mixture of 8 g dienyne (b.p. 131 – 133° at 4 mm, n_D^{20} 1.5580) and 40 ml concentrated hydrochloric acid was stirred 5 hours at 75 – 80°. Fractional distillation yielded 6 g of the original dienyne (I) and 1 g of a substance with b.p. 130 – 138° at 5 mm, n_D^{20} 1.5365.

c) A mixture of 15 g dienyne and 100 g formic acid was stirred 9 hours at 80 – 85°. Fractional distillation yielded 11 g of a mixture of cyclic ketones (VI) and (VII) with b.p. 137 – 139° at 3 mm, n_D^{17} 1.5380. (Cyclohydration did not occur when using a 6-fold quantity of formic acid for 5 hours at 70 – 75°. Nearly the whole of the dienyne was recovered unchanged.)

Cyclization of 1, 2-di-(Δ^1-cyclohexenyl)-ethanone (II). a) A mixture of 7 g dienone with a trace of chromanone (V) (b.p. 139 – 140° at 4 mm, n_D^{20} 1.5275) was stirred 3 hours at 80 – 90° with 11 g phosphoric acid (d 1.7). The product was worked up and fractionated to give 5 g of a mixture of cyclic ketones (VI) and (VII) with b.p. 145 – 147° at 5 mm, n_D^{20} 1.5360. (Cyclization does not occur under these conditions without stirring.)

b) 4.8 g dienone (b.p. 142 – 144° at 4 mm, n_D^{20} 1.5320) was treated with 5 g phosphoric acid (d 1.7) at room temperature for 22 hours. There was obtained 3 g of a mixture of the original dienone (II) and chromanone (V), b.p. 143 – 145° at 4 mm, n_D^{20} 1.5280; 2, 4-dinitrophenylhydrazones with m.p. 130 – 131° and 203 – 205°. No depression was seen in admixture with the above-described specimens. (Treatment of the dienone with phosphoric acid for 13 days at 15-20° gave a product considerably enriched with chromanone (V) (b.p. 145-150° at 5 mm, n_D^{22} 1.5190.)

Δ^3-Tetrahydrobenzaldehyde (IX) was prepared by condensation of butadiene and acrolein by the procedure previously described [16], and it had the following constants: b.p. 52 – 53° at 11 mm, n_D^{20} 1.4728.

Hexahydrobenzaldehyde (X) was prepared by hydrogenation of aldehyde (XI) [17] and had b.p. 62 – 63° at 25 mm, n_D^{20} 1.4512. Bromination and dehydrobromination of aldehyde (X) led to Δ^1-tetrahydrobenzaldehyde (XI) with b.p. 51 – 52° at 5 mm, n_D^{20} 1.4910 [17].

Preparation of propargyl bromide [19]. To 26.5 g phosphorus tribromide was added 2 – 3 drops of dry pyridine; while cooling with iced water, a solution of 27 g propargyl alcohol (dehydrated over calcium carbide) was added in the course of 2.5 hour. The reaction mixture was cooled for a further hour. Fractional distillation gave 29 g propargyl bromide with b.p. 82 – 84°, n_D^{20} 1.4940.

Synthesis of 1-Δ^1-cyclohexenyl-3-butyn-1-ol (XII). In the course of 30 min a solution of 11.0 g Δ^1-tetrahydrobenzaldehyde (XI), 11.7 g propargyl bromide, 15 ml absolute ether and 30 ml absolute tetrahydro-2-methylfuran was added dropwise to a boiling mixture of 7.1 g zinc (previously activated with 20% copper sulfate solution), 10 g mercuric chloride and 10 ml absolute ether. The reaction mixture was heated to 30 – 35°; the reaction then continued spontaneously for 40 min, after which the mass was heated at 40 – 45° for 30 min. The product (cooled with ice) was treated with 70 ml 10% acetic acid and then extracted with ether. The ethereal solution was washed with water and dried with sodium sulfate. Fractional distillation gave 9 g (66%) of carbinol in the form of a viscous, colorless liquid:

B.p. 89 – 90° at 2 mm, 93 – 94° at 3 mm, n_D^{20} 1.5090, d_4^{20} 0.9926, MR_D 45.8; Calc. 45.2

Found %: C 79.81, 79.88; H 9.16, 9.24. $C_{10}H_{14}O$. Calculated %: C 79.96; H 9.31.

Experiments on the oxidation of 1-Δ^1-cyclohexenyl-3-butyn-1-ol (XII). a) A mixture of 1 g carbinol, and 6 g freshly precipitated manganese dioxide in 40 ml absolute ligroine (b.p. 40–60°) was stirred 31 hours in an atmosphere of nitrogen at room temperature. Fractional distillation yielded 0.75 g of the original carbinol (b.p. 90 – 93° at 3 mm, n_D^{20} 1.5090).

b) A solution of 0.7 g chromic oxide, 0.5 ml concentrated sulfuric acid and 2 ml water was stirred with cooling into 1.1 g carbinol in 5 ml acetone in the course of 10 min. The reaction mixture was then stirred 20 min at this temperature. After working up, 0.7 g of the original carbinol (b.p. 92° at 4 mm, n_D^{20} 1.5060) was isolated. Oxidation with the same reagent and also with chromic oxide in glacial acetic acid at 18 – 20° gave the same results.

c) To the complex prepared from 10 g pyridine and 1 g chromic oxide was added a solution of 1.6 g carbinol in 10 ml pyridine; the mixture stood for 24 hours at 15 – 20°. Fractional distillation gave 0.7 g of the original carbinol with b.p. 94.5 – 95.5° at 3 mm, n_D^{19} 1.5075. In all of the cases a qualitative test for the carbonyl group gave negative results.

SUMMARY

1. Hydration of di-Δ^1-cyclohexenylacetylene in aqueous methanol in presence of mercuric sulfate gave 1, 2-(Δ^1-cyclohexenyl)-ethanone in high yield and it was shown to have the structure of a vinyl allyl ketone.

2. Heating of 1, 2-di-(Δ^1-cyclohexenyl)-ethanone with hydrochloric acid in isopropyl alcohol gave 2, 2--pentamethylene-hexahydro-4-chromanone in 65% yield; treatment of the latter with phosphoric acid converted it into a mixture of spiroindanones.

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REACTIONS OF SOME ANALOGS OF β-IONONE WITH GRIGNARD REAGENTS

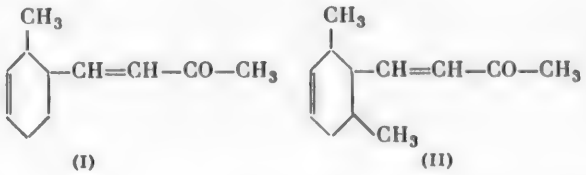
I. N. Nazarov, G. P. Kugatova and V. V. Lutsenko

Institute of Chemistry and Chemical Technology of the Academy of Sciences of the Lithuanian SSR

We previously [1] obtained analogs of β-ionone which can be utilized as intermediates in the synthesis of analogs and homologs of vitamin A; it was therefore of interest to make a closer study of their chemical properties and to examine their behavior in a number of chemical reactions. Another feature of the prepared ketones [1] that distinguishes them from the analogs of β-ionone themselves is that in the overwhelming majority of cases they possess a pleasant odor. From this aspect it was also of interest to use analogs of β-ionone as starting points for carbinols with different radicals and to examine the way in which the latter influence the odor of the new products.

In the present work we study the reactions of some analogs of β-ionone with Grignard reagents.

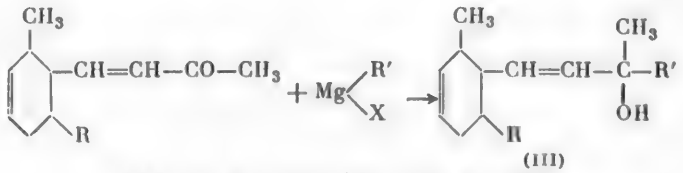
Investigations were carried out with organomagnesium compounds containing the methyl, ethyl and phenyl radicals and with ketones (I) and (II).



(I) (II)

The β-ionone analog (I) was prepared by condensation of 2-methyl-Δ^3-tetrahydrobenzaldehyde with acetone under the action of a little sodium hydroxide. 2-Methyl-Δ^3-tetrahydrobenzaldehyde was prepared by heating an equimolar mixture of acrolein and trans-piperylene in a metal ampoule for 2 hours at 180 – 190°.

In ethereal solution at the boiling point of ether, β-ionone analogs (I) and (II) react smoothly with Grignard reagents to give the corresponding tertiary alcohols (III) in 65 – 70% yield.



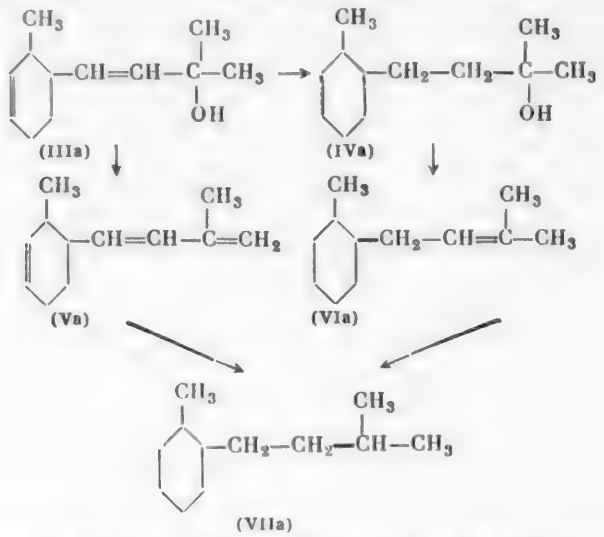
(III)

a) R = H, R′ = CH_3; d) R = CH_3, R′ = CH_3;
b) R = H, R′ = C_2H_5; e) R = CH_3, R′ = C_2H_5;
c) R = H, R′ = C_6H_5; f) R = CH_3, R′ = C_6H_5.

Under the conditions of the organomagnesium synthesis, β-ionone itself also gives, apart from the corresponding carbinols which are principal products of the reaction, ketones as a result of "abnormal" 1, 4-addition [2]. In the reaction with Grignard reagents of our selected β-ionone analogs, products of 1, 4-addition could not be isolated (treatment of the undistilled reaction product with a methanolic solution of semicarbazide led to separation in all cases not of the expected semicarbazones but of semicarbazide itself). The yield of alcohols (III) depends on the radical introduced and falls in passage from methyl to phenyl. If the decomposition temperature of the organomagnesium complex is above -10°, then in place of the expected carbinols we obtain difficultly separable mixtures of carbinols (III) and the corresponding hydrocarbons (V).

The tertiary alcohols (III) take up 2 moles of hydrogen on hydrogenation in methanol with palladium catalyst, and give the saturated carbinols (V).

Scheme for transformation of synthesized carbinols for variant a



Both the unsaturated (III) and the saturated (IV) carbinols differ from the hydrocarbons in possessing a pleasant, persistent odor reminiscent of citral.

Heating of carbinols (III) and (IV) with potassium bisulfate for 30 min at 130 – 140° and 60 – 70 mm leads to dehydration of the hydrocarbons (V) and (VI) respectively. But even two dehydrations with bisulfate or a second dehydration with other dehydrating agents do not give the pure hydrocarbon. There is always a residual content of 1 – 4% carbinols (III).

Analytically pure specimens of hydrocarbons (V) and (VI) can only be obtained by prolonged and repeated boilings of the product of dehydration with sodium.

On hydrogenation in methyl acetate with palladium catalyst, hydrocarbons (V) easily take up about two moles of hydrogen; the rate of hydrogenation then slows down appreciably, and completion of hydrogenation necessitates addition of platinum catalyst; the hydrogenation is then completed with formation of saturated hydrocarbons (VII) which are also obtained by hydrogenation of hydrocarbons (VI).

EXPERIMENTAL

Synthesis of ketone (I). 50 g 2-methyl-Δ^3-tetrahydrobenzaldehyde was dissolved in 100 ml freshly distilled acetone; in the course of 20 min at -4 to -2°, 4.3 g sodium hydroxide dissolved in a mixture of 385 ml acetone and 155 ml water was added with thorough stirring to the first solution. Stirring was then continued for 2.5 hours at room temperature. The reaction mixture was poured into water acidified with 8.5 ml concentrated hydrochloric acid. The product of extraction with ether, thrice washed with water, was dried with magnesium sulfate and distilled to give 41 g of a mixture of ketoalcohol and ketone with b.p. 112 – 113° (4 mm), n_D^{19} 1.4958.

A mixture of 41 g of the latter and 5 g of ignited pulverized potassium bisulfate was heated 30 min at 130 – 140° and 70 – 80 mm. After completion of heating, the vacuum was increased and the product distilled (b.p.

118° at 12 mm, n_D^{19} 1.4960), dried with magnesium sulfate and subjected to a second dehydration with 2 g potassium bisulfate under the same conditions, to yield 37 g ketone (I) with b.p. 98 – 99° (3.5 mm), n_D^{18} 1.4980.

Found %: C 80.36; H 9.75. $C_{11}H_{16}O$. Calculated %: C 80.48; H 9.75.

Ketone (II) was synthesized by the known method [1].

Synthesis of carbinols (III). To a solution of Grignard reagent, prepared from 2.8 g magnesium turnings and 17.1 g methyl iodide, in 240 ml anhydrous ether was added a solution of 17.5 g ketone (I) in 50 ml anhydrous ether. After 30 minutes' boiling, the reaction mixture was decomposed with 150 ml 30% ammonium acetate solution at -15 to -17°. The ethereal layer was collected and dried with anhydrous potassium carbonate. The solvent was distilled off and a solution of semicarbazide acetate was added to the residue. After standing 48 hours at room temperature, the precipitate of semicarbazide was filtered off. A large part of the methanol was distilled off in vacuo and more semicarbazide came down. The filtrate was treated with 250 ml water and 200 ml ligroine. The solution in ligroine was filtered through anhydrous potassium carbonate and stood overnight at below 0°. The semicarbazide coming down in this step was filtered and combined with the previous batches. Distillation of the filtrate gave 14.1 g carbinol (IIIa; R = H, R' = CH_3) with b.p. 87° (1.5 mm), n_D^{20} 1.4868.

Found %: C 80.13; H 11.04. $C_{12}H_{20}O$. Calculated %: C 80.00; H 11.11.

The other unsaturated carbinols (III) that were synthesized are set forth in Table 1.

Hydrogenation of unsaturated carbinols (III → IV). 7.5 g carbinol (IIIa; R = H, R' = CH_3) was hydrogenated with palladium catalyst in solution in 50 ml methanol. The catalyst was supported on calcium carbonate. Hydrogenation went sluggishly. Adams platinum catalyst [3] was added and hydrogenation was continued. A total of 1.95 liters H_2 was absorbed corresponding to the hydrogenation of two double bonds. The catalyst was filtered off, the solvent was distilled off, and the product of hydrogenation was distilled to give 6.5 g saturated carbinol (IVa; R = H, R^1 = CH_3 with b.p. 98° (6 mm), n_D^{18} 1.4710.

Found %: C 76.91; H 12.30. $C_{12}H_{22}O$. Calculated %: C 79.11; H 12.09.

The synthesized carbinols (IV) are set forth in Table 2.

Dehydration of unsaturated carbinols (III → V). A mixture of 14 g carbinol (IIIa) and 3 g ignited, pulverized potassium bisulfate was heated 30 min at 130 – 140° and 70 – 80 mm. The vacuum was then increased and the product was distilled (b.p. 110 – 113° at 20 mm, n_D^{16} 1.5058), dried with calcined magnesium sulfate and again dehydrated with 1.5 g potassium bisulfate under the above conditions. Yield 12.7 g unsaturated hydrocarbon (Va) with b.p. 98° (13 mm), n_D^{16} 1.5050, was obtained.

Found %: C 88.16; H 11.07. $C_{12}H_{18}$. Calculated %: C 88.88; H 11.12.

The remaining unsaturated hydrocarbons (V) that were prepared are set forth in Table 3.

Dehydration of saturated carbinols (IV → VI). A mixture of 6.4 g saturated carbinol (IVa) and 2.5 g ignited, pulverized potassium bisulfate was heated at 130 – 140° and 70 – 80 mm. The product was distilled (b.p. 106° at 18 mm, n_D^{18} 1.4850) and subjected to a second dehydration with 1.2 g potassium bisulfate under the same conditions. There was obtained 4.5 g saturated hydrocarbon (VIa) with b.p. 99° (18 mm), n_D^{19} 1.4860. The hydrocarbon was boiled in presence of metallic sodium and then distilled. B.p. 97° (18 mm), n_D^{20} 1.4880.

Found %: C 86.80; H 12.98. $C_{12}H_{22}$. Calculated %: C 86.74; H 13.25.

The other unsaturated hydrocarbons (VI) are set forth in Table 4.

Hydrogenation of unsaturated hydrocarbons (V → VII). 6 g hydrocarbon (Va) dissolved in 25 ml methyl acetate was hydrogenated in presence of palladium catalyst. Hydrogenation went sluggishly. Platinum catalyst was added and hydrogenation was continued. A total of 2.7 l. hydrogen was absorbed, corresponding to the hydrogenation of three double bonds. The catalyst was filtered off, the solvent was distilled off, and the product of hydrogenation was distilled to give 5.7 g saturated hydrocarbon (VIIa) with b.p. 88° (13 mm), n_D^{18} 1.4480.

Found %: C 85.40; H 14.05. $C_{12}H_{24}$. Calculated %: C 85.71; H 14.29.

TABLE 1

Unsaturated Carbinols (III)

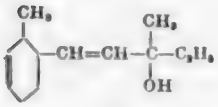
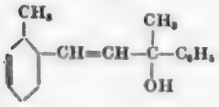
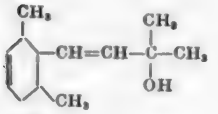
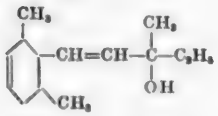
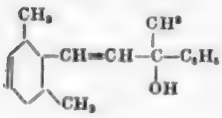
Formula	Yield (in %)	B. p. (pressure in mm)	Refractive index	% C		% H	
				found	calc.	found	calc.
	74.2	94° (2)	n_D^{20} 1.4855	80.25	80.41	11.20	11.30
	54.0	138 (0.4)	n_D^{20} 1.5380	84.20	84.29	9.19	9.09
	67.6	84 (1)	n_D^{22} 1.4811	80.49	80.41	11.65	11.29
	79.5	93—97 (1)	n_D^{22} 1.4837	80.54	80.77	11.64	11.54
	66.3	Does not distill	n_D^{20} 1.5357	84.30	84.37	9.69	9.37

TABLE 2

Saturated Carbinols (IV)

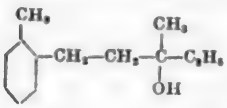
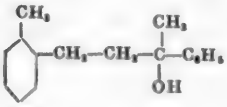
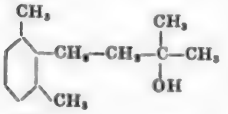
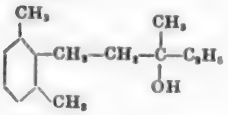
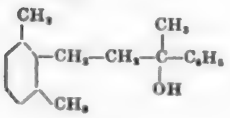
Formula	Yield (in %)	B. p. (pressure in mm)	Refractive index	% C		% H	
				found	calc.	found	calc.
	89.0	106° (5)	n_D^{18} 1.4651	79.06	78.78	12.78	13.33
	90.0	108 (0.1)	n_D^{17} 1.5150	83.08	82.92	10.72	10.52
	80.0	84—85 (1)	n_D^{22} 1.4670	78.99	78.78	12.78	13.13
	87.5	91—92 (1)	n_D^{22} 1.4713	79.23	79.24	12.82	13.20
	—	Does not distill	$n_D^{3.5}$ 1.5270	84.47	83.08	10.46	10.77

TABLE 3

Unsaturated Hydrocarbons (V)

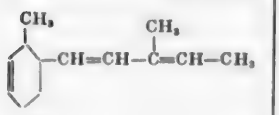
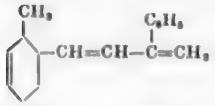
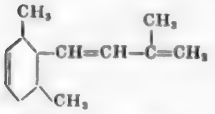
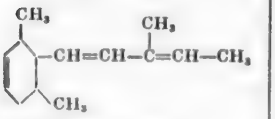
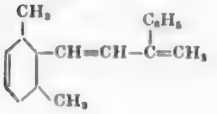
Formula	Yield (in %)	B. p. (pressure in mm)	Refractive index	% C		% H	
				found	calc.	found	calc.
	78.0	101° (9)	n_D^{20} 1.5038	88.70	88.63	11.20	11.27
	91.5	90 (2)	n_D^{18} 1.5170	91.03	91.07	8.69	8.92
	77.0	97 (10)	n_D^{20} 1.5010	88.55	88.63	11.60	11.36
	97.5	118 (12)	n_D^{20} 1.5013	86.93	88.44	11.70	11.58
	—	Does not distill	n_D^{18} 1.5650	88.51	90.75	9.57	9.24

TABLE 4

Unsaturated Hydrocarbons (VI)

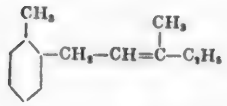
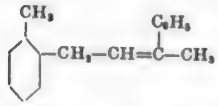
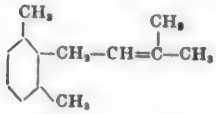
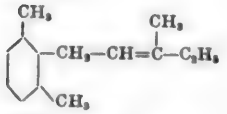
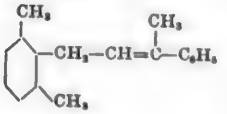
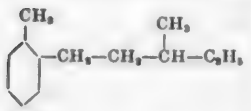
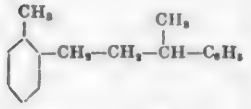
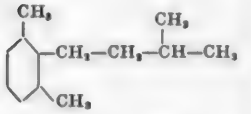
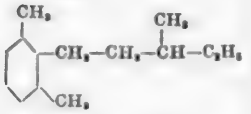
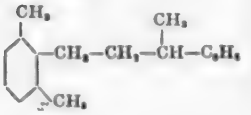
Formula	Yield (in %)	B.p. (pressure in mm)	Refractive index	% C		% H	
				found	calc.	found	calc.
	86.0	97° (12)	n_D^{18} 1.4760	86.53	86.66	12.95	13.33
	68.0	125 (2)	n_D^{20} 1.5074	—		—	
	61.2	101—108 (11)	n_D^{21} 1.4820	86.60	86.66	12.80	13.33
	62.2	118 (10)	n_D^{21} 1.4850	85.74	86.59	12.40	13.40
	—	128—130 (0.05)	n_D^{16} 1.5260	—	—	—	—

TABLE 5

Saturated Hydrocarbons (VII)

Formula	Yield (in %)	B. p. (pressure in mm)	Refractive index	% C		% H	
				found	calc.	found	calc.
	63.1	98° (10)	n_D^{16} 1.4530	85.78	85.71	14.24	14.29
	79.5	124 (2)	n_D^{17} 1.5070	88.58	88.70	11.30	11.30
	68.4	95—96 (10)	n_D^{23} 1.4540	85.69	85.71	14.10	14.29
	76.1	113 (11)	n_D^{24} 1.4550	85.06	85.71	14.29	14.28
	71.5	138—140 (1)	$n_D^{17.5}$ 1.5000	—		—	

Hydrogenation of unsaturated hydrocarbons (VI → VII). 3 g hydrocarbon (VIa) dissolved in 15 ml methanol was hydrogenated at first with palladium and later with platinum catalyst. 0.5 l. hydrogen was taken up, corresponding to hydrogenation of one double bond. After completion of hydrogenation, the catalyst was filtered off, the solvent was distilled off, and the product of hydrogenation was distilled to give 2.5 g saturated hydrocarbon (VIIa) with b.p. 87 – 89° (13 mm), n_D^{19} 1.4484.

Unsaturated hydrocarbons (VII) obtained from unsaturated hydrocarbons (V) and (VI) are set forth in Table 5.

SUMMARY

1. It was shown that the investigated analogs of β-ionone give products of normal addition with Grignard reagents.

2. A series of tertiary carbinols possessing a stable, pleasant odor reminiscent of citral was synthesized.

3. A study was made of the dehydration and hydrogenation of the carbinols, as well as of the hydrogenation of the hydrocarbons.

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SYNTHESIS AND CATALYTIC HYDROGENATION OF 2-METHYL-5-PHENYL-3-HEPTYNE-2, 5-DIOL

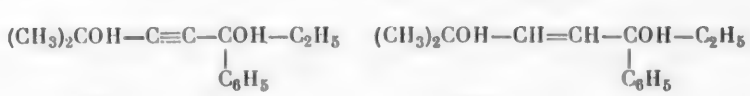
A. I. Nogaideli and Sh. V. Pichkhadze

Tbiliski State University

Numerous investigations have been carried out in the field of hydrogenation of acetylenic γ-glycols, in particular by Yu. S. Zal'kind and his school [1]. The catalysts used were mainly platinum black and colloidal palladium on wheat starch. It was found that in presence of colloidal palladium the addition of two atoms of hydrogen to the glycols takes place more intensively, and if the reaction is cut short the reaction products are olefinic compounds. In this way the selectivity of colloidal palladium prepared on wheat starch was demonstrated.

In the present work acetylenic γ-glycols were hydrogenated in presence of palladium supported on calcium carbonate. According to the literature palladium on calcium carbonate is a selective catalyst in the hydrogenation of monosubstituted ethynylcarbinols [2]. In presence of this catalyst, however, vinylethynyl carbinol forms a mixture of the starting substance, a dienic substance, and two isomeric olefinic carbinols [3]. In view of this behavior, it was desirable to ascertain the behavior of the catalyst in question in the hydrogenation of acetylenic γ-glycols.

The substance investigated was the unsymmetrical γ-glycol, 2-methyl-5-phenyl-3-heptyne-2, 5-diol (I), obtained from ethyl phenyl ketone and dimethylethynyl carbinyl magnesium bromide.



(I) (II)

It was found that palladium-on-calcium carbonate hydrogenates tetramethylbutynediol and 2-methyl-5-phenyl-3-heptyne-2, 5-diol to the stage of the olefinic derivatives; in this operation the first glycol adds on two atoms of hydrogen in 15 min while the second glycol requires 70 min (the glycol adds on 2 atoms of hydrogen slowly with gradual fall in rate of hydrogenation). It is established that the abrupt change in rate of hydrogenation after addition of two atoms of hydrogen in acetylenic γ-glycols is not the sole factor determining the formation of an olefinic bond. Our experiments demonstrate the selective character of palladium-on-calcium carbonate during hydrogenation of acetylenic γ-glycols.

The product of addition of two atoms of hydrogen is the olefinic glycol, 2-methyl-5-phenyl-3-heptene-2, 5-diol (II).

EXPERIMENTAL

Synthesis of 2-methyl-5-phenyl-3-heptyne-2, 5-diol (I). With iced-water cooling, dropwise addition was made of 26.4 g ethyl phenyl ketone diluted with an equal volume of dry ether (the ketone was prepared from benzoyl chloride and ethyl magnesium bromide in 21% yield, b.p. 217 – 218°) to dimethylethynyl carbinyl magnesium bromide prepared in the usual manner (from 9.6 g magnesium, 43.6 g ethyl bromide and 16.8 g dimethylethynyl carbinol). After the ketone had been added, mechanical stirring of the mixture was continued for another 36 hours at room temperature, after which the reaction mixture was decomposed with 15% ammonium chloride. After the usual working-up, the ethereal solution yielded 16 g colorless crystals, readily soluble in ether and alcohol, and sparingly soluble in benzene. M.p. 112 – 113° (from toluene).

Found %: C 77.24, 77.43; H 9.07, 7.83; OH 14.41. M 221 (acc. to Rast). $C_{14}H_{16}(OH)_2$. Calculated %: C 77.06; H 8.21; OH 15.50. M 218.

Hydrogenation of 2-methyl-5-phenyl-3-heptyne-2, 5-diol in presence of $Pd/CaCO_3$. The catalyst, 0.5 g, contained 0.6 mg palladium. The activity of the catalyst was checked by hydrogenation of tetramethylbutynediol, 0.01 mole of which added on 2 atoms hydrogen in the course of 15 min, after which period hydrogenation went very slowly (2 – 4 ml in 5 min). The reaction product was an ethylenic glycol with m.p. 69°.

Catalytic hydrogenation of 2.18 g 2-methyl-5-phenyl-3-heptyne-2, 5-diol was performed in 50 ml alcohol (730 mm, 18°) in presence of 0.6 mg palladium. After 70 min 225 ml hydrogen had been taken up (theoretical quantity 218 ml). Amounts taken up in successive periods of 5 min were 35.25, 25.20, 17.15, 13.10 ml, etc.

Hydrogenation yielded an olefinic glycol in the form of an oily, transparent liquid; it did not give a positive reaction for acetylene in the Bukhovts test and it decolorized bromine water.

B.p. 175 – 176° (3 – 4mm), d_4^{20} 0.9602, n_D^{20} 1.5170, MR_D 67.40; Calc. 67.73.

Found %: C 77.02; H 8.70; OH 16.45. M 223 (cryoscopic). $C_{14}H_{18}(OH)_2$. Calculated %: C 76.32; H 9.02; OH 15.45. M 220.

SUMMARY

1. The preparation and properties of 2-methyl-5-phenyl-3-heptyne-2, 5-diol are described.

2. The selective character of the hydrogenation of tetramethylbutynediol and of 2-methyl-5-phenyl-3-heptyne-2, 5-diol in presence of palladium on calcium carbonate was demonstrated.

3. It was established that 2-methyl-5-phenyl-3-heptyne-2, 5-diol hydrogenates more slowly than tetramethylbutynediol. The reaction rate slows down after addition of two atoms of hydrogen; the sole product is the ethylenic glycol 2-methyl-5-phenyl-3-heptene-2, 5-diol, which has not previously been described.

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INVESTIGATIONS OF CONJUGATED SYSTEMS

XCVIII. TELOMERIZATION OF BUTADIENE WITH CROTYL CHLORIDE AND 3-CHLORO-1-BUTENE •

A. A. Petrov, Kh. V. Bal'yan, L. I. Bunina-Krivorukova and T. V. Yakovleva

Leningrad Lensovet Institute of Technology

The systematic investigations undertaken in our laboratory of reactions of telomerization with participation of dienic hydrocarbons and alkenyl halides of the allyl type have revealed definite relations between the structure of the original dienes and halogenated derivatives and the character of the derived telomers [1 – 3].

It was established, for example, that butadiene forms considerably larger quantities of 1, 2-adducts than are formed by its homologs and substituted derivatives. However it was indicated in a frequently cited patent [4] that crotyl chloride and bromide add on the butadiene in the 1, 4-position. With the objective of resolving this contradiction and also of establishing in experiments with the simplest representative of the class whether allyl isomers give identical or different telomers, we carried out an investigation of the reactions of crotyl chloride and 3-chloro-1-butene with butadiene in presence of stannic chloride. The majority of the experiments were run with crotyl chloride.

The products of telomerization of butadiene with crotyl chloride were fractionated by distillation into adducts of the composition C_4H_7-C_4H_6-Cl, C_4H_7-$(C_4H_6)_2$-Cl and higher telomers. These in turn were resolved into two fractions A and B, although the character of the distillation indicated that more than two substances were involved. The experiments (see below) showed that fraction A consisted mainly of 3-chloro-1, 6-octadiene (1, 2-addition) and fraction B of 1-chloro-2, 6-octadiene (1, 4-addition). The ratio between fractions A and B was of the order of 1 : 1.3.

$CH_3-CH=CH-CH_2-CH_2-CHCl-CH=CH_2$ (I)

$CH_3-CH=CH-CH_2-CH_2-CH=CH-CH_2Cl$ (II)

$CH_3-CH=CH-CH_2-CH(CH_2Cl)-CH=CH_2$ (III)

$CH_2=CH-CH(CH_3)-CH_2-CHCl-CH=CH_2$ (IV)

$CH_2=CH-CH(CH_3)-CH_2-CH=CH-CH_2Cl$ (V)

$CH_2=CH-CH(CH_3)-CH(CH_2Cl)-CH=CH_2$ (VI)

• Dienic Compounds LXXIII. Reactions of dienes with halogenated derivatives. IX.

The infrared spectrum of fraction A (Table 3, Fig. 1, curve 1) contained strong frequencies of the vinyl grouping (6100, 1636, 1420, 986 and 920 cm^{-1}) together with the 1664 and 967 cm^{-1} frequencies which are characteristic of the -CH=CH- grouping.

In the Sommelet reaction with urotropine, fraction A participated to the extent of 25 – 30% [5], and a mixture of carbonyl compounds was isolated from the reaction products. The infrared spectrum of this mixture (Fig. 2, curve 2) contained, apart from carbonyl group frequencies, the frequencies of the -CH=CH- grouping (1664 and 965 cm^{-1}) as well as the frequencies of the vinyl group (6100, 986 cm^{-1}). Evidently we are dealing here with a mixture of aldehydes corresponding to chlorides (II) and (V), and possibly also with a mixture of ketones corresponding to chlorides (I) and (IV). The semicarbazone and 2, 4-dinitrophenylhydrazone prepared from the substance had low and gradual melting points.

The residue after the Sommelet reaction was the 1, 2-adduct substantially free of 1, 4-isomers. It distilled with a 1 – 2° range, hardly reacted with urotropine (5% after 100 hours), and on hydrogenation over $Pd/CaCO_3$ gave mainly n-octane. Treatment with urotropine, however, led to a decrease in the degree of unsaturation of the substance and to the appearance in the spectrum of a new and fairly strong frequency in the C-C vibration region (about 1120 cm^{-1}); the latter most probably resulted from partial isomerization of the carbon skeleton (formation of a cyclic chloride) [3].

Hydrogenation of the whole of fraction A over $Pd/CaCO_3$ also gave predominantly n-octane and a small quantity of chlorooctanes. Hydrogenation evidently goes in two directions. If attachment of chlorine at the hydrogen atom precedes hydrogenation of the conjugate double bond, then the end product is n-octane. But if addition of hydrogen at the above-mentioned double bond precedes substitution by chlorine, then the latter is stabilized and the end product is chlorooctane. Experiments showed that the first direction of the process predominates.

Judging by its constants, the octane formed by hydrogenation of fraction A is very nearly pure n-octane; however, it boiled over a fairly wide range and its spectrum contained frequencies absent from the the spectrum of n-octane and present in the spectrum of 3-methylheptane. The spectrum of the latter (Fig. 3, curve 6) differs from the spectrum of n-octane (curve 5) in containing fairly strong frequencies at 996 and 890 cm^{-1} and in respect to the considerable intensification of the 1150, 967 and 780 cm^{-1} frequencies. The 967 cm^{-1} frequency is particularly suitable for comparison. Judging by the relative intensity of all of these frequencies in the infrared spectrum of products of hydrogenation of fraction A, we can infer that they contain about 20% of 3-methylheptane.

3-Methylheptane could be obtained by hydrogenation of chlorides (IV), (V) and (III). The first route appears to us the more probable one on the basis of the considerations submitted below.

The composition of fraction B was established in similar fashion.

The infrared spectrum of fraction B contained strong frequencies of the -CH=CH- grouping (1664 and 965 cm^{-1}) together with weak frequencies of the vinyl group (Table 1, Fig. 1, curve 4). The fraction reacted with urotropine to the extent of 84% [5] to form mainly 2, 6-octadienal. Judging by the infrared spectrum, the substance contains a small admixture of a vinyl compound, evidently 5-methyl-2, 6-heptadienal (Fig. 2, curve 1); this is a most weighty piece of evidence in support of the hypothesis of formation of the isomeric chloride (V) during telomerization in addition to other products.

The residue after the Sommelet reaction contained very much more 1, 2-adduct than is present in the starting substance, since its infrared spectrum contained very much stronger vinyl frequencies than in the starting fraction (Fig. 1, curve 6). However, it distilled over a wide range and probably contained crotyl chloride dimer since about 31% chlorine was found in it. It is a curious fact that in this case the urotropine treatment of the substance led to development of a new frequency at about 1120 cm^{-1}.

Hydrogenation of fraction B over $Pd/CaCO_3$ gave n-octane with extremely small content of 3-methylheptane (less than 10%). The lower content of substances with a branched structure in fraction B in comparison with fraction A is entirely understandable: their boiling point is lower than that of straight chain compounds, so that fraction A will inevitably be enriched with them.

Ozonolysis of fraction B gave acetic, chloroacetic and succinic acids, and this behavior once again confirms its predominant content of chloride (II).

It has thus been established that in the first step of the telomerization of butadiene with crotyl chloride both 1, 4- and 1, 2-addition take place; in this reaction, products corresponding to the structure of 3-chlorobutene are formed in addition to products corresponding to the structure of crotyl chloride.

Subsequently we studied the telomers with the formula C_4H_7-$(C_4H_6)_2$-Cl. They were separated into two fractions by distillation.

The frequencies of the vinyl group were more conspicuous in the infrared spectrum of the first fraction (Fig. 4, curve 1). The latter reacted with urotropine to the extent of 30% in 50 hours, whereas the second fraction reacted to the extent of 50%. In the Sommelet reaction the second fraction gave a small yield of an aldehyde, evidently 2, 6, 10-dodecatrienal, together with some isomers with branched chains. The presence of the aldehyde group was confirmed by the infrared spectrum and by the derived 2, 4-dinitrophenylhydrazone.

After the Sommelet reaction the residue had an infrared spectrum with strong vinyl group frequencies (as in the other cases), and it developed a new frequency at about 1120 cm^{-1} (Fig. 4, curve 3).

It was thus shown that even more far-reaching telomerization likewise leads to addition of the halogenated derivatives both in the 1, 4- and 1, 2-positions.

The higher telomers were not studied.

Fractions A and B were isolated from the products of telomerization of butadiene with 3-chloro-1-butene. In quantity, constants and chemical properties (and consequently also in structure) they were very similar to the corresponding fractions of products of telomerization of butadiene with crotyl chloride. Their infrared spectra also corresponded (to within 2 – 3%, i.e., within the limits of plotting accuracy and reproducibility of the curves). The infrared spectra of the octanes prepared by hydrogenation of these fractions also agreed to within 2 – 3% with the spectra of the octanes obtained from the corresponding fractions of the telomer of butadiene with crotyl chloride.

These analogies also apply to the products of telomerization with the composition C_4H_7-$(C_4H_6)_2$-Cl.

The telomerization reaction is evidently of an ionic character in this case, and under the action of the catalyst both of the allylic isomers give the same common cation which possesses dual reactivity with more pronounced electrophilic activity in the 1 position.

$$\overset{\oplus}{\overbrace{CH_2{=}CH{=}CH}}-CH_3$$
$$\underset{1}{}\ \underset{2}{}\ \underset{3}{}\ \underset{4}{CH_3}$$

The present investigation had consequently established that the patent claims [4] do not correspond to the actual facts: telomerization of butadiene with its hydrochlorinated derivatives gives a mixture of 1, 4- and 1, 2--products.

In conclusion we maynote that telomerization of butadiene with allyl chloride under the same conditions gave only higher telomers.

EXPERIMENTAL

Crotyl chloride and 3-chloro-1-butene were prepared by addition of hydrogen chloride to technical butadiene. Although many investigators have carried out this reaction, the literature does not contain a detailed account of the procedure [6 – 8]. We proceeded in the following manner: butadiene (100 ml) was shaken in a closed, thick-walled bottle for 30 hours with 200 ml concentrated hydrochloric acid (d 1.19) in presence of 0.5 g $CuCl_2$ and 0.5 g Cu_2Cl_2. The upper layer of reaction products was washed with water and sodium carbonate solution and dried over $CaCl_2$; it was then distilled from a Widmer column. The yield of chlorides was usually about 70%. The ratio of crotyl chloride to its isomer was of the order of 2.5 – 3 to 1.

The constants of the chloro compounds were substantially the same as those reported in the literature [6 – 8].

	B.p.	d_4^{20}	n_D^{20}
Crotyl chloride	83.5 – 84°	0.9279	1.4350
3-Chloro-1-butene	64 – 64.5°	0.8978	1.4148

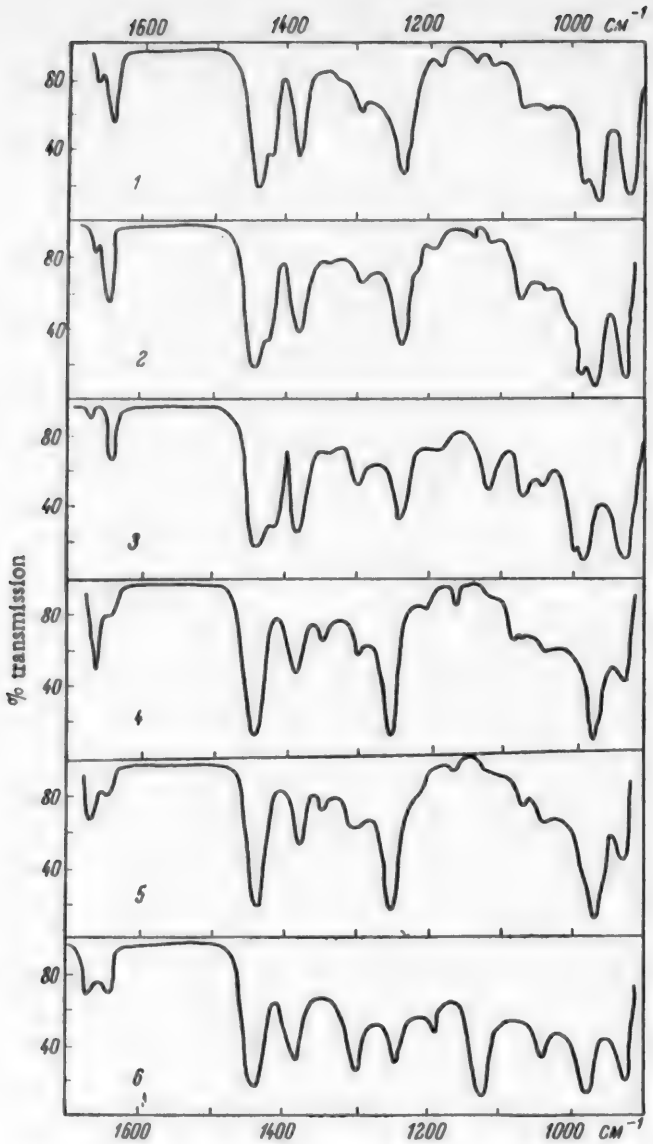

Fig. 1. Infrared transmission spectra. 1) Fraction A of telomer of crotyl chloride with butadiene; 2) fraction A of telomer of 3-chloro-1-butene with butadiene; 3) fraction A after treatment with urotropine; 4) fraction B of telomer of crotyl chloride with butadiene; 5) fraction B of telomer of 3-chloro-1--butene with butadiene; 6) fraction B after treatment with urotropine.

Telomerization was carried out in the apparatus previously described [3], usually until the specific gravity of the mixture had increased by about 0.09. With a greater increase of specific gravity the yield of initial products of telomerization fell. We usually carried out a reaction with 108 g (2 moles) butadiene, 181 g (2 moles) chloro compound and 250 ml methylene chloride. The duration of the reaction at 15 – 20° was about 3 hours. Reaction was stopped by addition of pyridine. A very small quantity of butadiene was lost during the experiment (the loss of weight usually did not exceed 7 g).

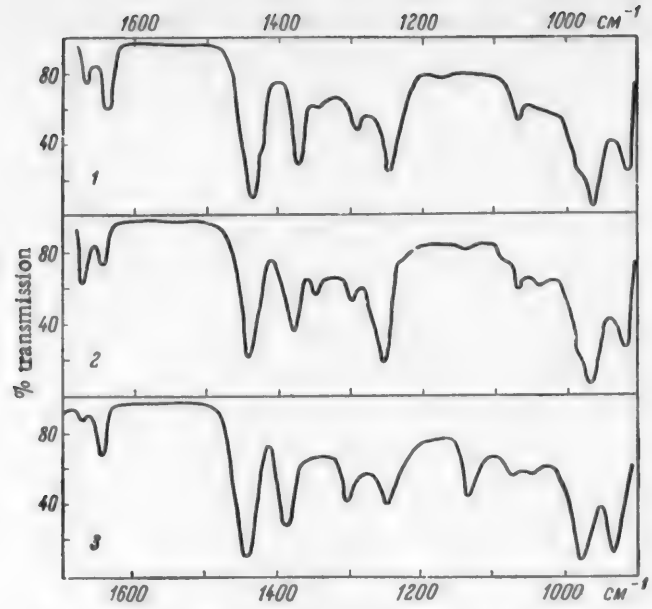

Fig. 2. Infrared transmission spectra. 1) 2, 6-Octadienal; 2) mixture of carbonyl compounds prepared from fraction A; 3) dodecatrienal.

In Table 1 are set forth the results of rough fractionation of the telomers obtained in several experiments with crotyl chloride and 3-chloro-1-butene. We carried out many similar experiments. Results were reproducible.

Investigation of the telomer of butadiene with crotyl chloride. The first fraction with b.p. up to 110° at 5 mm (Table 1) was precision-fractionated in a Widmer column. Results of one experiment in which the specific gravity increased by 0.07 are presented in Table 2.

TABLE 1

Alkenyl chloride*	Increase in specific gravity	Results of fractionation at 5 mm: frac. up to 110° (in g)	Results of fractionation at 5 mm: residue (in g)
Crotyl chloride	0.075	51.8	74.3
	0.091	66.3	84.2
	0.120	45.2	110.0
3-Chloro-1-butene	0.065	53.9	67.0

The infrared spectra of fractions A and B are detailed in Table 3 and plotted in Fig. 1.

Investigation of fraction A. a) The Sommelet reaction. Reaction of 27 g fraction A with 9 g urotropine under the previously described conditions [1, 2] gave 2 g carbonyl compounds and 17 g residue.

Found for carbonyl compounds:

B.p. 68 – 71°(10 mm), d_4^{20} 0.8686, n_D^{20} 1.4712.

Found %: C 76.67, 76.60; H 9.70, 9.41. $C_8H_{12}O$. Calculated %: C 77.37; H 9.74.

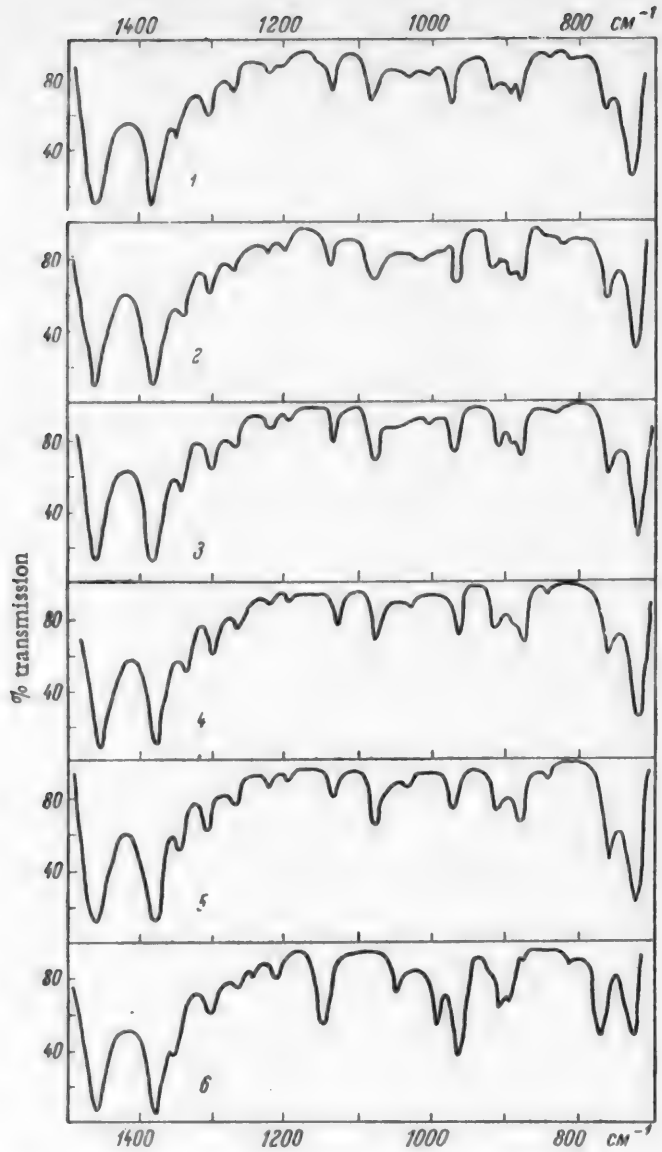

Fig. 3. Infrared transmission spectra of hydrocarbons. 1) Products of hydrogenation of fraction A of telomer obtained from crotyl chloride; 2) products of hydrogenation of fraction A of telomer obtained from 3-chloro-1-butene; 3) products of hydrogenation of fraction B of telomer obtained from crotyl chloride; 4) products of hydrogenation of fraction B of telomer obtained from 3-chloro-1-butene; 5) n-octane; 6) 3-methylheptane.

Infrared spectrum: 920 (strong), 978 (very strong), 996 (strong), 1007 (medium), 1035 (weak), 1100 (medium), 1138 (very strong), 1300 (medium), 1382 (medium), 1421 (strong), 1444 (strong), 1463 (strong), 1635 (very strong), 1680 (very strong) cm^{-1}.

Semicarbazone, m.p. about 124° (from aqueous alcohol); 2, 4-dinitrophenylhydrazone, m.p. 110 – 115° (from aqueous alcohol).

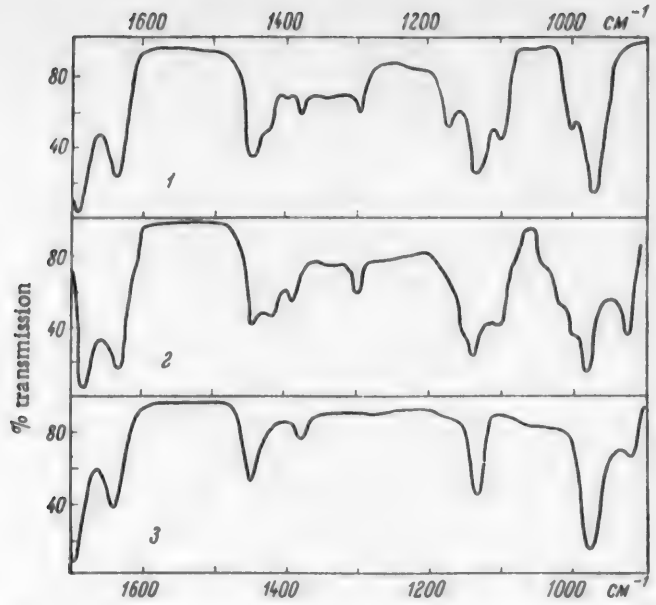

Fig. 4. Infrared spectrum of telomers of composition C_4H_7-$(C_4H_6)_2$-Cl. 1) 2nd Fraction; 2) 4th fraction; 3) same fraction after treatment with urotropine

TABLE 2

Characteristics of Products of Telomerization of Butadiene with Crotyl Chloride in Presence of Tin Chloride •

Fraction (at 10 mm)	Weight (in g)	d_4^{20}	n_D^{20}	Reactive chlorides[5] (in %)••	Found (%)•••		
					C	H	Cl
До 52°	1.1	—	—	—	—	—	—
52—54 (А)	5.7	0.9127	1.4570	27.5 28.4	67.03 67.05	9.20 9.40	24.18
54—58	2.0	—	—	—	—	—	—
58—62	2.2	—	—	—	—	—	—
62—66 (Б)	7.2	0.9253	1.4675	83.8 84.1	66.70 66.44	9.41 9.40	24.43
66—75	3.3	—	—	—	—	—	—
Residue	9.3	—	—	—	—	—	—
Total	30.5 g						

• 32.5 g taken for fractionation.

•• Method proposed for determination of primary allylic chlorides in presence of tertiary chlorides which do not react with urotropine. In the present case it only gives a rough idea of the content of primary chlorides since secondary chlorides do react with urotropine in the Sommelet reaction even though very sluggishly.

••• $C_8H_{13}Cl$. Calculated %: C 66.42; H 9.06; Cl 24.52.

The residue after the Sommelet reaction had the following constants:

B.p. 51 – 52° (10 mm), d_4^{20} 0.9159, n_D^{20} 1.4550.

Found %: Cl 25.72. $C_8H_{13}Cl$. Calculated %: Cl 25.52.

TABLE 3

Infrared Transmission Spectra of Telomers•

Fraction A		Fraction B	
from crotyl chloride	from 3-chloro-1-butene	from crotyl chloride	from 3-chloro-1-butene
1664 (w)	**1664 (w)**	**1664 (m.s.)**	**1664 (v.s.)**
1636 (m.s.)	**1636 (m.s.)**	1636 (w)	1636 (w)
1440 (v.s.)	**1440 (v.s.)**	1440 (v.s.)	1440 (v.s.)
1420 (s)	**1420 (s)**	—	—
1375 (s)	**1375 (s)**	1375 (s)	1375 (s)
1336 (m.s.)	**1336 (m.s.)**	1345 (m.s.)	1345 (m.s.)
1295 (m.s.)	**1295 (m.s.)**	1295 (m.s.)	1295 (m.s.)
1250 (s)	**1250 (s)**	1250 (v.s.)	1250 (v.s.)
1177 (w)	**1179 (w)**	1194 (w)	1194 (w)
1132 (w)	**1132 (w)**	1155 (w)	1155 (w)
1105 (w)	**1105 (w)**	1075 (w)	1075 (w)
1063 (m.s.)	**1066 (m.s.)**	1064 (m.s.)	1064 (m.s.)
1033 (m.s.)	**1033 (m.s.)**	1035 (m.s.)	1035 (m.s.)
985 (v.s.)	**985 (v.s.)**	—	—
965 (v.s.)	**965 (v.s.)**	964 (v.s.)	964 (v.s.)
922 (v.s.)	**922 (v.s.)**	925 (s)	925 (s)

• Values in bold type are characteristic frequencies of the main substance in each fraction.

TABLE 4

Characteristics of Telomers of Butadiene and Crotyl Chloride with the Formula $C_4H_7(C_4H_6)_2$-Cl•

Fraction (at 3 mm)	Wt. (in g)	d_4^{20}	n_D^{20}	Reactive chlorides (in %)	Found (%) ••		
					C	H	Cl
To 92°	4.2	—	—	—	—	—	—
92—94	13.5	0.9371	1.4770	32.91, 34.60	70.46, 70.41	9.68, 9.64	20.08
94—102	3.3	—	—	—	—	—	—
102—104	15.4	0.9382	1.4830	48.7, 52.6	71.63, 71.53	9.77, 9.72	18.90
104—120	3.2	—	—	—	—	—	—
Residue	7.5	—	—	—	—	—	—
Total	47.1						

• 48.0 g taken for fractionation

•• $C_{12}H_{19}Cl$. Calculated %: C 72.52; H 9.64; Cl 17.84.

Reactive chlorides found: 4 – 7%. Dienes found (Kaufmann method): 67.3, 67.2%. •

The infrared spectrum of the substance did not differ from that of the original fraction apart from the slight lowering of intensity of the 970 cm^{-1} frequency and the development of the 1120 cm^{-1} frequency.

• 75.6 and 77.1% dienic chlorides were found in the original fraction. In both of the cases the results are too low because the Kaufmann method does not give correct values in such cases and can only be applied for comparison.

TABLE 5

Characteristics of Products of Telomerization of Butadiene with 3-Chloro-1-butene in Presence of Tin Chloride. •

Fraction (at 10 mm)	Wt. (in g)	d_4^{20}	n_D^{20}	Reactive chlorides (in %)	Found (%) ••		
					C	H	Cl
До 52°	1.8	—	—	—	—	—	—
52—54 (А)	6.7	0.9079	1.4565	21.4, 20.4	68.47, 68.25	9.41, 9.23	22.69
54—58	2.4	—	—	—	—	—	—
58—62	2.2	—	—	—	—	—	—
62—66 (Б)	9.0	0.9206	1.4690	79.2, 83.1	66.64, 66.61	9.19, 9.00	24.60
66—75	1.9	—	—	—	—	—	—
Residue	9.5	—	—	—	—	—	—
Total	33.5						

• 35.0 g taken for fractionation.

•• $C_8H_{13}Cl$. Calculated %: C 66.42; H 9.06; Cl 24.52.

TABLE 6

Characteristics of Telomers of Butadiene with 3-Chloro-1-butene of the Composition C_4H_7-$-(C_4H_6)_2$-Cl •

Fraction (at 3 mm)	Wt. (in g)	d_4^{20}	n_D^{20}	Reactive chlorides (in %)	Found (%)		
					C	H	Cl
92—94°	7.2	0.9347	1.4762	36.3, 36.2	70.23, 70.39	9.72, 9.78	19.70
102—104	3.2	0.9366	1.4830	54.2, 53.3	71.78, 71.78	9.84, 9.89	18.60

• 22 g taken for fractional distillation.

b) Hydrogenation. Hydrogenation of 27.5 g of substance in 250 ml methyl alcohol over 50 g $Pd/CaCO_3$ led to absorption of 12,070 ml H_2 (767 mm, 19°), equivalent to 80%. Hydrogenation was performed in two steps. The products of reaction were distilled with steam. In the residue was found 5.89 g (87.3%) chlorine. The products of reaction were separated from the distillate by salting-out with saturated $CaCl_2$ solution and were fractionated in a Widmer column to give 13.5 g (80%) n-octane and 5.4 g chlorine-containing residue from which 3.3 g chlorooctanes (impure) were isolated.

Found for n-octane: b.p. 122 – 126°, d_4^{20} 0.7058, n_D^{20} 1.3988; these values are close to the literature data [9]. The infrared spectrum is plotted in Fig. 3.

Judging by the spectrum, this specimen of octane contains not less than 20% 3-methylheptane (confirmed by examination of mixtures of n-octane and 3-methylheptane).

The commerical n-octane that we used had the constants:

B.p. 125 – 126°, d_4^{20} 0.7022, n_D^{20} 1.3972.

Infrared spectrum: 1462 (very strong), 1382 (very strong), 1348 (strong), 1305 (medium), 1270 (medium), 1223 (weak), 1198 (weak), 1136 (weak), 1080 (medium), 1028 (weak), 967 (medium), 916 (medium), 890 (medium), 877 (weak), 842 (weak), 762 (strong), 722 (strong) cm^{-1}.

3-Methylheptane was prepared by hydrogenation over $Pd/CaCO_3$ of 3-methylheptene obtained by dehydration (distillation with oxalic acid) of 3-methyl-3-heptanol. The latter had been obtained from butyl bromide and methyl ethyl ketone (Grignard reaction).

3-Methylheptane had the following constants:

B.p. 119°, d_4^{20} 0.7045, n_D^{20} 1.4000.

Infrared spectrum: 1451 (very strong), 1375 (very strong), 1352 (strong), 1297 (medium), 1266 (weak), 1246 (weak), 1215 (weak), 1150 (medium), 1077 (medium), 994 (strong), 965 (strong), 907 (medium), 894 (medium), 873 (very weak), 817 (very weak), 770 (strong), 726 (strong) cm^{-1}.

Found for chlorooctanes:

B.p. 52 – 53° (10 mm), n_D^{20} 1.4310, in close agreement with the literature [10].

Found %: C 65.77, 65.67; H 11.27, 11.38; Cl 22.01. $C_8H_{17}Cl$. Calculated %: C 64.62; H 11.53; Cl 23.85.

Investigation of fraction B. a) Sommelet reaction. From 20 g fraction B under the previously described conditions was obtained 7 g (41%) 2, 6-octadienal, probably contaminated with 5-methyl-2, 6-heptadienal (less than 10%), and 2.3 g residue. Reaction was carried out for 100 hours.

The following constants were found for 2, 6-octadienal:

B.p. 71–71.5° (10 mm), d_4^{20} 0.8705, n_D^{20} 1.4738, MR_D 40.08; Calc. 38.22.

Found %: C 77.53, 77.57; H 9.51, 9.57. $C_8H_{12}O$. Calculated %: C 77.37; H 9.74.

Infrared spectrum: 974 (very strong), 1004 (medium), 1113 (medium), 1134 (very strong), 1174 (medium), 1300 (medium), 1382 (medium), 1401 (weak), 1425 (medium), 1444 (strong), 1456 (strong), 1640 (strong), 1696 (very strong) cm^{-1}.

Semicarbazone, m.p. 179° (from aqueous alcohol). Colorless leaflets.

Found %: N 23.24, 23.44. $C_9H_{15}ON_3$. Calculated %: N 23.19.

4-Nitrophenylhydrazone, m.p. 130° (from aqueous alcohol). Yellow crystals.

Found %: N 15.64, 15.77. $C_{14}H_{17}O_2N_3$. Calculated %: N 16.21.

2. 4-Dinitrophenylhydrazone, m.p. 150° (from alcohol). Orange crystals.

Found %: N 18.42, 18.64. $C_{14}H_{16}O_4N_4$. Calculated %: N 18.41.

b) Hydrogenation. Reduction of 25 g fraction B over 50 g $Pd/CaCO_3$ in methanol solution (250 ml) consumed 10,200 ml hydrogen (759.6 mm, 20°), equivalent to 80%. Found in solution 6.10 g chlorine (92.5%). There was obtained 13 g n-octane (82%) and 1.9 g residue containing chlorine.

Constants of n-octane:

B.p. 124.5 – 125.5°, d_4^{20} 0.7040, n_D^{20} 1.3982.

The infrared spectrum is plotted in Fig. 3 (curve 3).

From the residue was isolated a main fraction (0.9 g) with the following constants:

B.p. 60 – 65° (10 mm), d_4^{20} 0.9036, n_D^{20} 1.4415.

Found %: C 67.54, 67.30; H 11.57, 11.88; Cl 21.26. $C_8H_{17}Cl$. Calculated %: C 65.62; H 11.53; Cl 23.85.

c) Ozonization of 5 g fraction B gave acetic acid (b.p. 40 – 46° at 6 mm; detected by the Feigl test [11]), chloroacetic acid (m.p. 61° from ligroine; same melting point in mixed melting test) and succinic acid (m.p. 183°, same melting point in mixed melting test).

Investigation of higher telomers. The combined residues from several experiments after distillation of the lower telomers (Table 2) were subjected to fractionation in a Widmer column. Results are presented in Table 4.

The analytical data indicate the presence of crotyl chloride dimers ($C_8H_{14}Cl_2$) in the products. Calculated %: C 53.05; H 7.79; Cl 39.16).

The infrared spectra of the 2nd and 4th fractions are plotted in Fig. 4 (curves 1 and 2).

By the Sommelet reaction with urotropine, the 4th fraction yielded an aldehyde, presumably 2,6,10-dodecatrienal, contaminated by branched-chain isomers.

B.p. 142 – 146° (10 mm), d_4^{20} 0.8820, n_D^{20} 1.4850. MR_D 57.92; calc. 56.24.

Found%: C 81.50, 81.39; H 10.39, 10.13. $C_{12}H_{18}O$. Calculated%: C 80.66; H 10.18.

Infrared spectrum: 916 (weak), 970 (very strong), 1128 (strong), 1380 (weak), 1445 (strong), 1458 (strong), 1638 (strong), 1694 (very strong) cm^{-1}.

2, 4-Dinitrophenylhydrazone m.p. 126 – 128° (from alcohol).

Found %: N 15.62, 15.55. $C_{18}H_{22}O_4N_4$. Calculated %: N 15.63.

Telomerization of butadiene with 3-chloro-1-butene. These experiments were carried out under the same conditions as with crotyl chloride. Results of fractional distillation of the low-boiling portion of the telomers (increase in specific gravity 0.07) are presented in Table 5.

The infrared spectra of fractions A and B are set forth in Table 3 and plotted in Fig. 1 (curves 2 and 4).

Hydrogenation of fraction A gave n-octane with the following constants:

B.p. 124 – 125.5°, d_4^{20} 0.7072, n_D^{20} 1.3990.

Judging by the infrared spectrum, the substance does not differ from the n-octane obtained by reduction of fraction A of the telomer of butadiene with crotyl chloride.

Reduction of fraction B gave n-octane with the following constants:

B.p. 125 – 125.7°, d_4^{20} 0.7036, n_D^{20} 1.3980.

Judging by the infrared spectrum the substance does not differ from a pure preparation and from the n-octane obtained by reduction of fraction B from the products of telomerization of butadiene with crotyl chloride.

Results of fractional distillation of the residues (Table 5) from several experiments are presented in Table 6.

The infrared spectra of the fractions set forth in Table 6 did not differ from the spectra of the same fractions obtained from the telomer of butadiene with crotyl chloride.

The infrared spectra of all of the compounds were plotted with the IKS-14 spectrophotometer with an NaCl prism. In the case of the halogenated derivatives the layer thickness was 0.032 mm, in the case of the hydrocarbons it was 0.102 mm.

The spectral region of about 6100 cm^{-1} was plotted with the IKS-12 spectrograph with a glass prism and a layer thickness of 1-2 mm. Data are given in the text.

SUMMARY

1. The telomerization of butadiene with the products of its hydrochlorination – crotyl chloride and 3-chloro-1-butene – was investigated in presence of tin chloride.

2. In both cases products of 1, 4-addition as well as of 1, 2-addition were formed, the former predominating.

3. The two allylic isomers – crotyl chloride and 3-chloro-1-butene – form telomers that are closely similar in properties and structure and contain predominantly chlorides with a normal structure.

4. On the basis of the above results, it is concluded that the process is an ionic one and that a cation with dual reactivity common to both of the chlorides is formed.

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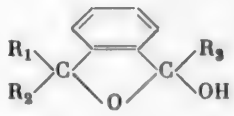
INVESTIGATIONS ON HYDROXYPHTHALANS 3,3-DIMETHYL-1--(p-TOLYL)-1-HYDROXYPHTHALANA AND 3,3-DIMETHYL-1--(p-ANISYL)-1-HYDROXYPHTHALAN

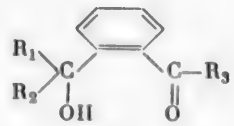
L. A. Pavlova

Leningrad Lensovet Institute of Technology

Substituted hydroxyphthalans can react both in the cyclic form (I) and in the form of acylbenzyl alcohols (II) [1 – 4]. Condensations of 1, 3, 3-triphenyl-1-hydroxyphthalan with phenol and aromatic amines [5], reduction of this hydroxyphthalan with formic acid to 1, 3, 3-triphenylphthalan [6], and formation of alkylidenephthalans on dehydration of 1-alkyl-1-hydroxyphthalans [4, 7] can serve as examples of reactions proceeding with the cyclic form (I). At the same time the interaction of 1, 3, 3-triphenyl-1-hydroxyphthalan with 2, 4-dinitrophenylhydrazone [6], formation of diphenylanthrone from 1, 3, 3-triphenyl-1-hydroxyphthalan and of o-isopropenylbenzophenone from 3, 3-dimethyl-1-phenyl-1-hydroxyphthalan [2] are only possible with participation of the opened, hydroxyketonic form (II).



(I)



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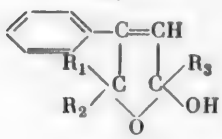

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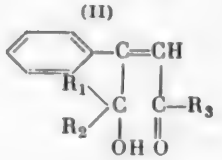


(IV)

In structure the substituted hydroxyphthalans are extremely similar to the 2-hydroxy-2, 5-dihydrofurans (III) which were first prepared and studied by E. D. Venus-Danilova and co-workers [8 – 10]. It was found that hydroxydihydrofurans give two series of derivatives. On the one hand these substances react in the cyclic form (III) with facile formation of ethers of the type of ketals which enter into reaction with substances containing labile hydrogen atoms and are converted on reduction into compounds of the 2, 5-dihydrofuran series; on the other hand under the action of reagents at the carbonyl group, hydroxydihydrofurans form derivatives of olefinic γ-ketoalcohols (IV). An interesting property of hydroxydihydrofurans is their ability to form salts. It was shown that in salt-forming reactions the hydroxydihydrofurans behave like carbonium bases.

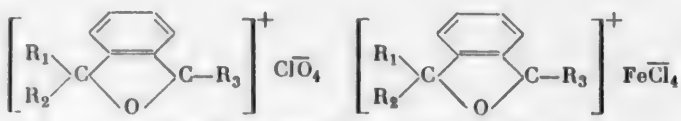
The similarity between the structure and properties of 1-hydroxyphthalans and 2-hydroxy-2, 5-dihydrofurans indicated that the hydroxyphthalans should resemble hydrofurans in manifesting basic properties. This hypothesis was checked by preparation of two previously unknown hydroxyphthalans – 3, 3-dimethyl-1-(p-tolyl)-1-hydroxyphthalan (I, $R_3 = C_6H_4CH_3$) and 3, 3-dimethyl-1-(p-anisyl)-1-hydroxyphthalan (I, $R_3 = C_6H_4OCH_3$).

Recently A. Fabrytsy [11] synthesized the already known 3, 3-dimethyl-1-phenyl-1-hydroxyphthalan and closely studied its properties.

3, 3-Dimethyl-1-(p-tolyl)-1-hydroxyphthalan and 3, 3-dimethyl-1-(p-anisyl)-1-hydroxyphthalan were prepared, on the same lines as 3, 3-dimethyl-1-phenyl-1-hydroxyphthalan [2], from dimethylphthalide, and p--tolyl magnesium bromide and p-anisyl magnesium bromide respectively.

As had been anticipated, the synthesized hydroxyphthalans possessed basic properties. The perchlorate, ferrichloride and stannichloride were prepared from 3, 3-dimethyl-1-(p-tolyl)-1-hydroxyphthalan; the perchlorate, ferrichloride and picrate were prepared from 3, 3-dimethyl-1-(p-anisyl)-1-hydroxyphthalan.

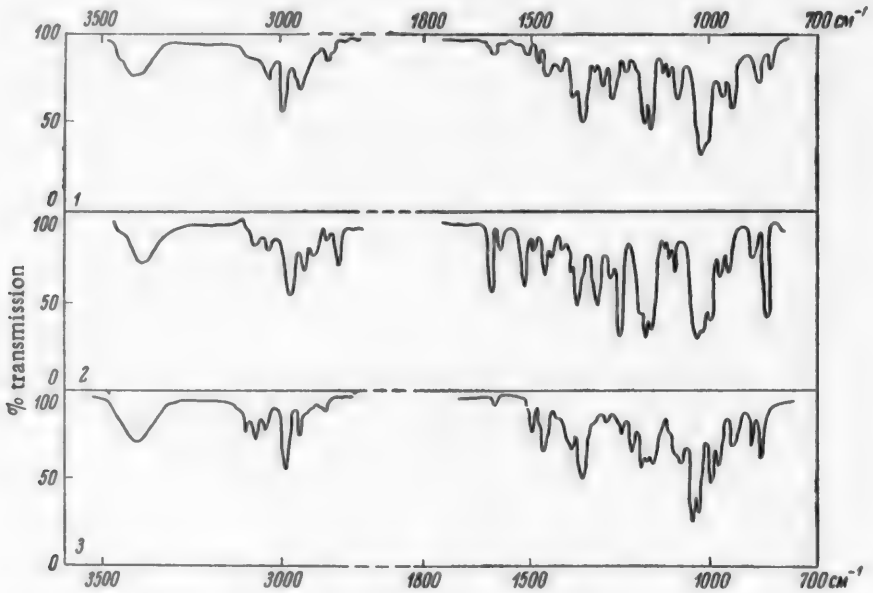
By analogy with salts of hydroxydihydrofurans [10], the structure of the prepared salts can be represented by the following formulas:



$R_1 = R_2 = CH_3$, $R_3 = n\text{-}C_6H_4\text{—}CH_3$, $n\text{-}C_6H_4\text{—}OCH_3$.

In comparison with hydroxydihydrofurans, the hydroxyphthalans are less basic, possibly due to shortening of the chain of conjugated double bonds, which influences the stability of the carbonium ion. The synthesized hydroxyphthalans were also condensed with phenylmethylpyrazolone and carbonyl derivatives – 2, 4-dinitrophenylhydrazones and semicarbazones.

Infrared spectra of the following substances were plotted: 3, 3-dimethyl-1-(p-tolyl)-1-hydroxyphthalan, 3, 3-dimethyl-1-(p-anisyl)-1-hydroxyphthalan, and (for comparison) 5, 5-dimethyl-2, 4-diphenyl-2-hydroxy-2, 5-dihydrofuran • (see diagram).



Infrared transmission spectra. 1) 3, 3-Dimethyl-1-(p-tolyl)-1-hydroxyphthalan; 2) 3, 3-dimethyl-1-(p-anisyl)-1-hydroxyphthalan; 3) 5, 5-dimethyl-2, 4-diphenyl--2-hydroxy-2, 5-dihydrofuran.

Carbonyl group frequencies were not observed in the spectra of these compounds. This shows that the predominant form of hydroxyphthalans and hydroxydihydrofuran is the cyclic form (I, III).

• The spectra were plotted and investigated by T. V. Yakovleva to whom we convey our profound thanks.

The infrared spectra were obtained with the IKS-14 spectrophotometer in the region up to 4μ with a LiF prism, and later with a NaCl prism. Layer thickness was 250μ. The substance was examined in 2.5% solution in carbon tetrachloride.

It was previously shown [9, 10] that 2-hydroxy-2, 5-dihydrofurans are 5-membered analogs of compounds of the chromenol, flavenol and xanthydrol series. This series can now be supplemented by the family of substituted hydroxyphthalans.

EXPERIMENTAL •

3, 3-Dimethyl-1-(p-tolyl)-1-hydroxyphthalan

The hydroxyphthalan was prepared from dimethylphthalide and p-tolyl magnesium bromide in 76% yield. Colorless crystals with m.p. 125 – 126° (from ether – ligroine mixture). The substance is soluble in ether, benzene, methyl and ethyl alcohols. It dissolves with a light-yellow color in concentrated sulfuric acid.

Found %: C 80.30, 80.30; H 7.21, 7.00; OH 6.57. M 258. $C_{17}H_{18}O_2$. Calculated %: C 80.28; H 7.13; OH 6.68. M 254.3.

Infrared spectrum: 824 (very weak), 866 (weak), 940 (medium), 959 (weak), 1019 (very strong), 1092 (medium), 1110 (very weak), 1118 (very weak), 1159 (strong), 1175 (strong), 1232 (very weak), 1272 (weak), 1295 (very weak), 1318 (very weak), 1363 (medium), 1379 (medium), 1409 (very weak), 1458 (weak), 1483 (very weak), 1512 (very weak), 1611 (very weak), 2870 (weak), 2939 (medium), 2995 (strong), 3034 (medium), 3084 (very weak), 3400 (medium) cm^{-1}.

The perchlorate was obtained under conditions described in the literature for tri-p-methoxyphenylcarbinol [12]. To a solution of 1.25g hydroxyphthalan in 15 ml acetic anhydride was added dropwise 1.8 ml 68% perchloric acid. The first drops of perchloric acid colored the solution red, and the color deepened with progressive addition of acid and then changed to yellow. The rapidly deposited precipitate was filtered, washed with glacial acetic acid on the filter and then recrystallized from glacial acetic acid. Yield 1.25 g (76%) yellow needles with m.p. 177 – 178°.

Found %: C 60.72, 60.71; H 5.16, 5.23; Cl 10.50, 10.94. $C_{17}H_{17}O_5Cl$. Calculated %: C 60.62; H 5.09; Cl 10.53.

The ferrichloride separated when concentrated hydrochloric acid was added to an alcoholic solution of 0.5 g of the hydroxyphthalan and 0.5 g ferric chloride. There was obtained 0.85 g (97%) of fine, light-yellow crystals with a lilac tinge. M.p. 136 – 137°. Slight resinification was observed on recrystallization of the substance from alcohol, and this was probably the cause of the slight deviation in the analytical results.

Found %: C 47.32, 47.31; H 4.54, 4.37; Cl 34.02, 34.01; Fe 12.07. $C_{17}H_{20}OCl_4Fe$. Calculated %: C 46.94; H 3.94; Cl 32.60; Fe 12.84.

Stannichloride. To a solution of the hydroxyphthalan in 5 ml methylene chloride was added a solution of 0.5 g stannic chloride in 1.5 ml methylene chloride. Hydrogen chloride was passed through the solution. A greenish-yellow precipitate came down; it was well washed on the filter with absolute ether. M.p. 184 – 185°. Yield 0.3 g (60%).

Found %: C 48.49, 48.75; H 4.47, 4.62; Cl 25.83, 26.07; Sn 13.50, 13.59. $C_{34}H_{38}O_4Cl_6Sn$. Calculated %: C 48.46; H 4.55; Cl 25.26; Sn 14.09.

The 2, 4-dinitrophenylhydrazone was formed by running together an alcoholic solution of 0.5 g of the hydroxyphthalan with an alcoholic solution of 0.5 g 2, 4-dinitrophenylhydrazine to which was added 0.5 ml concentrated hydrochloric acid. The orange precipitate, m.p. 218 – 219° (decomp.), was nearly insoluble in alcohol and soluble in ether. Yield 0.5 g (58%).

Found %: C 63.31, 63.23; H 5.28, 5.29; N 12.81, 12.84. $C_{23}H_{22}O_5N_4$. Calculated %: C 63.58; H 5.10; N 12.90.

• Students V. I. Vyshkvar' and A. V. Gagin participated in the experimental work.

Semicarbazone. To a solution of 0.7 g hydroxyphthalan in 3.5 ml alcohol was added an alcoholic solution of 1 g semicarbazide acetate and 3 drops glacial acetic acid. Stout, tabular crystals of the semicarbazone came down on the following day. M.p. 143 – 144° (from 80% alcohol).

Found %: N 13.76, 13.69. $C_{18}H_{21}O_2N_3$. Calculated %: N 13.49.

Condensation of 3, 3-dimethyl-1-(p-tolyl)-1-hydroxyphthalan with phenylmethylpyrazolone was performed under the conditions described in the literature for 4, 4'-tetramethyldiaminodiphenylcarbinol [13]. 0.5 g of the hydroxyphthalan and 0.5 g phenylmethylpyrazolone were dissolved in 15 ml methyl alcohol and heated 4 hours on a water bath. After 2 days the solution deposited crystals. The substance was soluble in ether and benzene, less readily soluble in methyl and ethyl alcohols, ligroine and carbon tetrachloride. M.p. 185 – 186° (from aqueous acetone).

Found %: C 77.34, 77.04; H 6.56, 6.49; N 7.28. $C_{27}H_{26}O_2N_2$. Calculated %: C 77.20; H 6.38; N 6.83.

3, 3-Dimethyl-1-(p-anisyl)-1-hydroxyphthalan

p-Anisylhydroxyphthalan was prepared by the organomagnesium synthesis from dimethylphthalide and p-bromoanisole. Yield 35%. M.p. 107 – 108° (from a mixture of ether and ligroine). Soluble in alcohol, ether and benzene, less soluble in ligroine and carbon tetrachloride. Soluble in concentrated sulfuric acid with a green color, and in concentrated hydrochloric acid with a yellow color.

Found %: C 75.68, 75.50; H 6.49, 6.58; OH 7.08. M 268. $C_{17}H_{18}O_3$. Calculated %: C 75.53; H 6.71; OH 6.44. M 270.3.

Infrared spectrum: 835 (strong), 866 (weak), 933 (weak), 937 (weak), 959 (weak), 989 (strong), 1024 (very strong), 1092 (weak), 1107 (very weak), 1124 (very weak), 1160 (strong), 1170 (strong), 1180 (strong), 1248 (very strong), 1270 (weak), 1302 (medium), 1363 (medium), 1378 (medium), 1413 (very weak), 1445 (very weak), 1461 (weak), 1483 (very weak), 1510 (weak), 1586 (very weak), 1611 (strong), 2838 (medium), 2870 (very weak), 2909 (weak), 2933 (medium), 2976 (very strong), 3035 (weak), 3077 (weak), 3400 (medium) cm^{-1}.

The perchlorate was prepared by addition of 2 ml 68% perchloric acid to a solution of 1.35 g hydroxyphthalan in 15 ml acetic anhydride. Long, bright-yellow needles came down the next day and turned orange on drying. Yield 0.6 g perchlorate with m.p. 145 – 146°. An additional 1.1 g was isolated from the mother liquor. Yield nearly quantitative.

Found %: C 57.70, 57.71; H 5.29, 5.28; Cl 10.20, 10.26. $C_{17}H_{17}O_6Cl$. Calculated %: C 57.88; H 4.86; Cl 10.07.

Ferrichloride. To a solution of 0.5 g hydroxyphthalan in alcohol was added a saturated alcoholic solution of ferric chloride and concentrated hydrochloric acid. Stout, yellow, crystals of the ferrichloride came down at once. M.p. 136 – 137° (from methyl alcohol). Yield 0.75 g (90%).

Found %: C 45.59, 45.24; H 3.75, 3.86; Cl 31.21, 31.38; Fe 12.04, 12.08. $C_{17}H_{16}O_2Cl_4Fe$. Calculated %: C 45.28; H 3.80; Cl 31.44; Fe 12.38.

Picrate. a) 0.3 g p-anisylhydroxyphthalan and 0.3 g picric acid were mixed well and fused in a wide test tube. The resulting dark mass was triturated in benzene. Orange-yellow crystals were formed with m.p. 152 – 153° (from alcohol). b) 0.3 g hydroxyphthalan and 0.3 g picric acid were dissolved in the minimum quantity of methyl alcohol. The solution was gently heated. An orange precipitate soon came down and was thoroughly washed with benzene. M.p. 152 – 153°. Yield 0.5 g (94%).

Found %: C 57.02, 57.12; H 4.22, 4.26; N 8.96. $C_{23}H_{19}O_9N_3$. Calculated %: C 57.38; H 3.97; N 8.72.

The 2, 4-dinitrophenylhydrazone was formed in 72% yield on mixing an alcoholic solution of the hydroxyphthalan with an alcoholic solution of 2, 4-dinitrophenylhydrazine to which had been added a few drops of concentrated hydrochloric acid. Dark-yellow crystals with m.p. 148 – 150°.

Found %: C 61.32, 61.61; H 4.73, 4.98; N 12.27, 12.39. $C_{23}H_{22}O_6N_4$. Calculated %: C 61.33; H 4.92; N 12.44.

The semicarbazone separated on standing from an alcoholic solution of the hydroxyphthalan and semicarbazide acetate to which 3 drops of glacial acetic acid had been added. Fine, lustrous crystals. M.p. 171 – 172° (from aqueous alcohol).

Found %: N 13.06, 12.90. $C_{18}H_{21}O_3N_3$. Calculated %: N 12.84.

Condensation of 3, 3-dimethyl-1-(p-anisyl -1-hydroxyphthalan with phenylmethylpyrazolone. 0.5 g of the hydroxyphthalan and 0.5 g phenyldimethylpyrazolone were dissolved in 12 ml methyl alcohol and heated 4 hours on a water bath at boiling. After 2 days the solution deposited a finely crystalline substance which after two recrystallizations from aqueous acetone had m.p. 168 – 169°.

Found %: C 75.81, 75.68; H 6.44, 6.52; N 6.66, 6.52. $C_{27}H_{26}O_3N_2$. Calculated %: C 76.04; H 6.14; N 6.59.

SUMMARY

1. The previously undescribed 3, 3-dimethyl-1-(p-tolyl)-1-hydroxyphthalan and 3, 3-dimethyl-1-(p--anisyl)-1-hydroxyphthalan were synthesized. Using these compounds as examples, it was shown that substituted 1-hydroxyphthalans manifest basic properties.

2. In structure and properties the substituted 1-hydroxyphthalans resemble 2-hydroxy-2, 5-dihydrofurans; they are five-membered analogs of compounds of the chromenol, flavenol and xanthydrol series.

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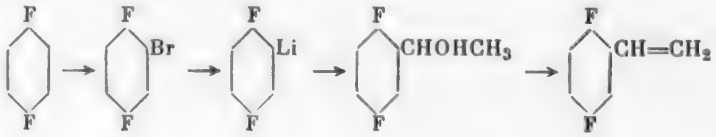
FLUORINATED STYRENES IV. 2, 5-DIFLUOROSTYRENE AND 2, 5-DIFLUORO-β-FLUOROSTYRENE

T. V. Talalaeva, G. V. Kazennikova and K. A. Kocheshkov

L. Ya. Karpov Institute of Physical Chemistry

We developed a procedure for synthesis of styrenes containing two fluorines in the nucleus and applied it to the synthesis of 2, 4-difluorostyrene [1]. In the present paper we described the synthesis of 2, 5-difluorostyrene which was effected by the following scheme:



The starting 1, 4-difluorobenzene was obtained from p-phenylenediamine hydrochloride. This compound was bis-diazotized at a temperature of about -15° in concentrated nitric acid solution and was converted at -15° into the bis-diazonium borofluoride. Thermal decomposition of the latter gave 1, 4-difluorobenzene.

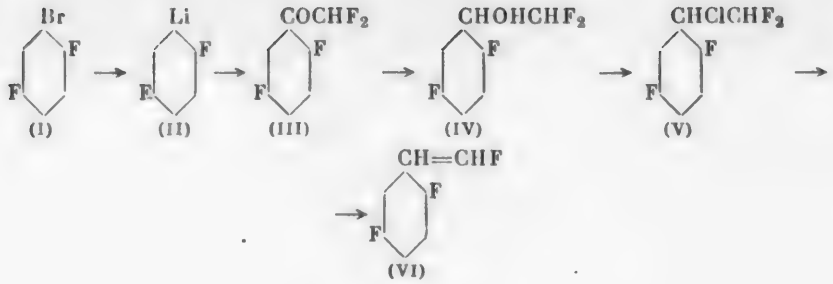
Contrary to the assertions by Schiemann and Pillarsky [2] of the impossibility of effecting the bis-diazotization of p-phenylenediamine hydrochloride in portions larger than 18 g, we smoothly diazotized batches of up to 100 g, although it was necessary to keep within the above temperature limits.

In agreement with the literature reports [3], bromination of 1, 4-difluorobenzene goes with a small yield of 2, 5-difluorobromobenzene, and 2, 5-difluoro-1, 4-dibromobenzene is formed as a secondary product in considerable quantity.

We acted on 2, 5-difluorobromobenzene with n-butyllithium (or ethyllithium) in ethereal solution at a temperature of about -70° and so obtained 2, 5-difluorophenyllithium in nearly quantitative yield. Condensation of this compound at -70° with acetaldehyde gave 2, 5-difluorophenylmethyl carbinol. We dehydrated this carbinol under the usual conditions with potassium bisulfate and obtained 2, 5-difluorostyrene.

1, 4-Difluorobenzene does not condense with acetyl chloride in carbon disulfide under the action of aluminum chloride, and we were unable to obtain 2, 5-difluoroacetophenone by this route. It may be noted that 1, 4-dichlorobenzene likewise does not enter into this reaction [4].

As starting substance for preparation of 2, 5-difluoro-β-fluorostyrene we took 2, 5-difluorobromobenzene (I). Treatment of the latter with ethyllithium at -70° gave 2, 5-difluorophenyllithium (II). This was subsequently condensed at the same temperature with difluoroacetic acid to give 2, 5-difluoro-ω, ω-difluoroacetophenone (III). The latter was reduced with sodium borohydride to 2, 5-difluorophenyl-difluoromethylcarbinol (IV). By means of thionyl chloride the carbinol was converted to 2, 5-difluoro-β, β-difluoro-α-chloroethylbenzene (V), which was then treated with zinc in a medium of acetamide to give 2, 5-difluoro-β-fluorostyrene (VI).



EXPERIMENTAL

1. Preparation of bis-p-phenylenediazonium borofluoride. To a mixture of 400 ml hydrochloric acid (d 1.18) and 640 g ice at a temperature of -24° to -15° was added a cooled solution of 120 g of a cooled suspension of 72 g p-phenylenediamine hydrochloride in 100 ml hydrochloric acid. After 5 min, 400 ml cooled hydrofluoboric acid (prepared from 40% hydrofluoric acid) was run at -15° into the light-yellow solution of p-phenylenediamine bisdiazotate, and the mass was stood (under cooling) for 15 min. All operations were performed with vigorous stirring. The precipitated lustrous salt was quickly suction-filtered on a broad, porous glass filter, washed several times with cooled alcohol and ether, and dried in the air. Yield 80 g.

2. Preparation of 1, 4-difluorobenzene. Bis-p-phenylenediazonium borofluoride was thermally decomposed in 200 g portions. Yield of 1, 4-difluorobenzene about 45 g (60%), b.p. 88.3°, n_D^{18} 1.4420. The literature gives [2]: n_D^{18} 1.4422, b.p. 88 – 88.6°.

3. Preparation of 2, 5-difluorobromobenzene. 1, 4-Difluorobenzene was brominated in 50 g batches under the usual conditions (at 30 – 35°) in presence of iron. Yield of 2, 5-difluorobromobenzene up to 50%. B.p. 54° (22 mm), n_D^{20} 1.5092. The literature gives [3]: b.p. 58 – 58.5° (20 mm), n_D^{20} 1.5086.

2, 5-Difluoro-1, 4-dibromobenzene was obtained as a secondary product in quantity of 24 – 25 g with m.p. 65°.

4. Preparation of 2, 5-difluorophenylmethylcarbinol. 230 ml 0.8 N ethereal solution of n-butyllithium was placed in a special reactor for work at low temperatures under nitrogen, and cooled to -75°. With energetic stirring addition was then made in the course of 30 min of the equimolar quantity of 2, 5-difluorobromobenzene (35.5 g) in 20 ml ether at a temperature not higher than -60°. The mass was then cooled at -75°, an excess (13.5 g) of acetaldehyde was added in the course of 15 min to the transparent, light-yellow solution of 2, 5-difluorophenyllithium, with maintenance of the temperature at not higher than -60°; the mass was then stirred for another 10 min, cooled to -74° and poured onto ice containing 5% hydrochloric acid. After ether extraction and the usual working-up, there was obtained 15 g of 2, 5-difluorophenylmethylcarbinol (57.3%) with b.p. 92.5 – 93.0° (15 mm), n_D^{20} 1.4839.

Found %: F 24.50, 24.34. $C_8H_8OF_2$. Calculated %: F 24.04.

5. Preparation of 2, 5-difluorostyrene. Reaction was performed with simultaneous distillation of the resulting styrene derivative in vacuo (110 mm). Components taken were 15.8 g 2, 5-difluorophenylmethylcarbinol, 1 g freshly prepared potassium bisulfate and 0.3 g copper powder. The reaction mixture at 110 mm was immersed in a bath heated to 140°, and the bath temperature was then raised to 150° in the course of 10 min; at this temperature the styrene started to distill and continued to do so for about 1 hour; at the end of the experiment the bath temperature was raised to 220°. The styrene was extracted with ether, washed with iced water and dried. Distillation gave about 7.5 g (53.6%) of 2, 5-difluorostyrene, b.p. 56° (30 mm), n_D^{20} 1.4982.

Found %: F 27.46, 27.54. $C_8H_6F_2$. Calculated %: F 27.13.

6. Preparation of 2, 5-difluoro-ω, ω-difluoroacetophenone (III). A solution of 2, 5-difluorophenyllithium was prepared in the course of 35 min from 225 ml 0.7 N ethyllithium, diluted with 100 ml absolute ether, and 32.8 g 2, 5-difluorobromobenzene [3] under nitrogen. The mixture was vigorously stirred during the preparation and the temperature was kept at about -70°. At the same temperature, in course of 30 min, 8.2 g difluoroacetic acid [5] in 25 ml ether was run in, and stirring continued for another 30 min. Decomposition was effected by

pouring the mass on to ice containing dilute hydrochloric acid. The ethereal solution was separated and worked up in the usual manner to give 6.5 g (40%) 2, 5-difluoro-ω, ω-difluoroacetophenone (III), b.p. 93 – 94° (25 mm), n_D^{20} 1.4665.

Found %: F 38.77, 38.87. $C_8H_4OF_4$. Calculated %: F 39.58.

7. Preparation of 2, 5-difluorophenyl-difluoromethylcarbinol (IV). In the course of 25 min 26.7 g 2, 5--difluoro-ω, ω-difluoroacetophenone (III) in an equal volume of methanol was stirred into a solution of 2.28 g sodium borohydride in 15 ml water and 2 ml 2 N sodium hydroxide. The temperature of the reaction mixture was allowed to rise to 50°; the mixture was then stirred 1 hour at room temperature, decomposed under cooling, poured into 200 ml 10% sodium hydroxide, and extracted with ether. The usual working-up gave 24.3 g (89.5%) 2, 5-difluorophenyl-difluoromethylcarbinol with b.p. 109° (25 mm), n_D^{20} 1.4595.

Found %: F 38.62, 38.76. $C_8H_6OF_4$. Calculated %: F 39.18

8. Preparation of 2, 5-difluoro- β, β-difluoro-α-chloroethylbenzene (V). Reaction was performed under the usual conditions: 11.6 g carbinol (IV) was treated with 14.1 g thionyl chloride in dry pyridine (9.4 g). After the usual working-up, there was obtained 10.1 g (80.8%) 2,5-difluoro-β, β-difluoro-α-chloroethylbenzene with b.p. 85° (25 mm), n_D^{20} 1.4613.

Found %: F 35.24, 35.45; Cl 16.10, 15.95. $C_8H_5ClF_4$. Calculated %: F 35.94; Cl 16.77.

9. Preparation of 2, 5-difluoro-β-fluorostyrene (IV). A mixture of 16.8 g 2, 5-difluoro-β, β-difluoro-α--chloroethylbenzene, 35 g acetamide, 8.2 g zinc powder and 0.3 g copper powder was heated 1 hour on a bath at a temperature of 125°, then cooled to 40°, and poured into iced water containing 8 ml concentrated nitric acid. The mass was extracted with ether, and the ethereal solution was washed, dried and distilled. There was obtained 6.3 g (50%) 2, 5-difluoro-β-fluorostyrene, b.p. 81 – 82° (60 mm), n_D^{20} 1.4841.

Found %: F 35.97, 35.88. $C_8H_5F_3$. Calculated %: F 36.06.

SUMMARY

1. 2, 5-Difluorostyrene was prepared for the first time.

2. A method for preparation of 2, 5-difluorophenyllithium was developed.

3. 2, 5-Difluoro-β-fluorostyrene was prepared for the first time.

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SOME ESTERS OF DIALKYLARSENIOUS ACIDS

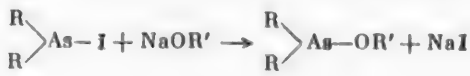
Gil'm Kamai and B. D. Chernokal'skii

Kazan S. M. Kirov Institute of Chemical Technology

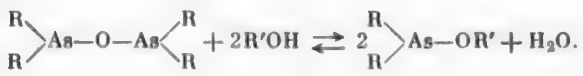
Little work has been done on esters of dialkylarsenious acids. Only four representatives of this class have hitherto been reported in the literature – the methyl, ethyl, n-butyl and n-octyl esters of di-n-butylarsenious acid, the synthesis and some properties of which were first described by K. I. Kuz'min [1].

It appeared to us not without interest to prepare esters of other dialkylarsenious acids and to study their properties. We used the following two routes for the synthesis of these esters:

a) Reaction of dialkyliodoarsine with the appropriate sodium alkoxides

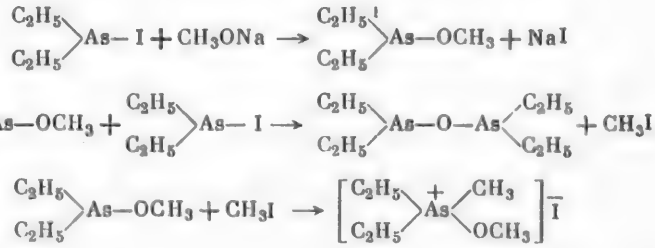


b) Heating of bis(dialkylarsine)oxide with alcohols in presence of calcium carbide as a water-removing agent



The second method gives the best results.

Reaction of dialkyliodoarsine with sodium alkoxide does not go to completion, and the resulting ester is therefore contaminated with the starting iodo compound. Difficulties consequently arise in the purification of the ester. Secondary products are another complication. For example the reaction of diethyliodoarsine with sodium methoxide led to formation of crystals whose analysis indicated the presence of methyl diethylmethoxyarsonium iodide. To account for the formation of this compound, we assume that not all of the diethyliodoarsine reacted during the synthesis and that the latter enters into intermolecular reaction with the methyl ester of diethylarsenious acid, while the separated methyl iodide adds on to the arsenious ester.



The synthesized alkyl esters of dialkylarsenious acids and some of their properties are presented in Table 1.

TABLE 1

Preparation No.	Formula of ester	B.p. (pressure in mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	% As found	% As calc.	Yield (in %)
1	$(C_2H_5)_2As{-}OC_2H_5$	141—142° (10)	1.1114	1.4621	43.82	43.65	42.14	42.31	76.2
2	$(C_2H_5)_2As{-}OC_3H_7$	50—52 (10)	1.0859	1.4613	48.59	48.43	38.99	39.00	59.0
3	$(C_2H_5)_2As{-}OC_4H_9$	72—72.5 (13)	1.0688	1.4608	52.90	53.05	35.84	36.34	77.7
4	$(C_3H_7)_2As{-}OC_2H_5$	66—68 (12)	1.0636	1.4620	53.28	53.05	35.94	36.34	61.3
5	$(CH_3)(C_4H_9)As{-}OC_2H_5$	51—5—52 (10)	1.0826	1.4607	48.67	48.43	39.14	39.00	55.9
6	$(CH_3)(C_4H_9)As{-}OC_3H_7$	83 (10)	1.0470	1.4603	57.76	57.66	33.95	34.06	85.4

TABLE 2

Preparation No.	Formula	B. p. (pressure in mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	% As found	% As calc.	Yield (in %)
1	$(C_2H_5)_2As{-}O{-}As(C_2H_5)_2$	107.5—110° (15)	1.3036	1.5123	65.16	65.30	—	—	86.0
2	$(C_3H_7)_2As{-}O{-}As(C_3H_7)_2$	139—142 (12)	1.1855	1.5000	83.90	83.75	43.65	44.16	68.1
3	$(CH_3)(C_4H_9)As{-}O{-}As(CH_3)(C_4H_9)$	126.5—127.5 (11)	1.2290	1.5017	74.62	74.54	47.58	48.18	63.9

The esters are readily mobile, colorless liquids. In the air they oxidize and are readily hydrolyzed by moisture to the corresponding dialkylarsenious acids. Heating with alkyl halides in sealed ampoules leads to deposition of crystals, but we did not examine these closely.

EXPERIMENTAL

The starting bis(dialkylarsine)oxides were obtained by saponification of dialkyliodoarsines with aqueous sodium hydroxide. Dialkyliodoarsines were synthesized from arsenic trioxide and alkyl iodides by the reaction of Meyer and Auger [2–8]. Boiling points: ethyliodoarsine 123–125° (11 mm); n-propyliodoarsine 132–134° (13 mm); n-butyliodoarsine 146–148° (13 mm); the latter has d_4^{20} 2.4456; diethyliodoarsine 82–84° (18 mm), d_4^{20} 1.8936; di-n-propyliodoarsine 100–103° (10 mm), d_4^{20} 1.7082; methyl-n-butyliodoarsine 87.5–89° (12 mm), d_4^{20} 1.7802.

Some constants of bis(dialkylarsine)oxides are presented in Table 2.

Preparation of ethyl ester of diethylarsenious acid. 28.6 g sodium ethoxide and 400 ml dry diethyl ether were placed in a three-necked flask fitted with stirrer, reflux condenser and dropping funnel; 109 g diethyliodoarsine was then stirred into the suspension. The reaction mixture was then boiled on a water bath for 4 hours; after cooling, the precipitate was filtered and washed with ether. After the solvent had been driven off, the residue was distilled in vacuo. Two distillations gave 56.5 g (76.2%) of product.

B.p. 141 – 142°, d_4^{20} 1.1114, n_D^{20} 1.4621, MR_D 43.82, Calc. 43.65.

Found %: As 42.14. $C_6H_{15}OAs$. Calculated %: As 42.31.

Preparation of ethyl ester of methyl-n-butylarsenious acid. 96 g methylbutyliodoarsine and 23.8 g sodium ethoxide were reacted as in the preceding experiment and gave 37.6 g (55.9%) of the ethyl ester of methyl-n-butylarsenious acid.

B.p. 51.5 – 52° (10 mm), d_4^{20} 1.0826, n_D^{20} 1.4607, MR_D 48.67; Calc. 48.43.

Found %: As 39.14. $C_{17}H_{17}OAs$. Calculated %: As 39.00.

The ester is a readily mobile, colorless liquid.

Preparation of propyl ester of diethylarsenious acid. An adapter with a wad of filter paper containing 20 g calcium carbide was fitted to a three-necked flask. The top of the adapter was closed with a stopper to which a reflux condenser was attached so that the condensed liquid entered the wad. Into the flask were charged 50.8 g bis(diethylarsine)oxide and 60 g absolute propyl alcohol. The contents of the flask were boiled 3 hours on a glycerol bath. After the excess of alcohol had later been distilled off, the residual liquid was vacuum-distilled. Four distillations gave 38.6 g n-propyl ester of diethylarsenious acid.

B.p. 50 – 52° (10 mm), d_4^{20} 1.0859, n_D^{20} 1.4613, MR_D 48.59; Calc. 48.43.

Found %: As 38.99. $C_7H_{17}OAs$. Calculated %: As 38.98.

The remaining alkyl esters of dialkylarsenious acid were synthesized in similar fashion. Results of the investigations are presented in Table 1.

Interaction of diethyliodoarsine with sodium methoxide. 24.3 g sodium methoxide and 350 ml dry diethyl ether were placed in a three-necked flask fitted with reflux condenser, stirrer and dropping funnel. 117 g diethyliodoarsine was stirred in and the mixture was heated 6.5 hour on a water bath. After cooling, the precipitate was filtered and the solvent was distilled off. Further distillation gave 48.3 g of a 142 – 159° fraction, and crystals came down in the distillation flask and receiver. The crystals were filtered, washed with dry diethyl ether and dried in a vacuum-desiccator. M.p. 283 – 284° (decomp.).

Found %: As 24.56, 24.52. $C_6H_{16}OAsI$. Calculated %: As 24.48.

Judging by the arsenic content, the separated substance is methyldiethylmethoxyarsonium iodide.

The methyl ester of diethylarsenious acid could not be isolated from the remaining liquid in the pure form.

Hydrolysis of propyl ester of diethylarsenious acid. 0.9 g propyl ester of diethylarsenious acid was diluted in a test tube with 10 ml dry ether and stood in the air. After a short time, stout, flat crystals came down. These were separated from the liquid, washed with ether and dried in vacuo. The crystals melted at 134.5 – 136°.

The literature [2] gives m.p. 133 – 134°.

Found %: As 44.96. $C_4H_{11}O_2As$. Calculated %: As 45.12.

SUMMARY

1. The following substances were prepared for the first time: the ethyl, n-propyl and n-butyl esters of diethylarsenious acid; the ethyl ester of di-n-propylarsenious acid; the ethyl and n-butyl esters of methyl-n-butylarsenious acid.

2. Alkyl esters of dialkylarsenious acids react with alkyl halides to form onium compounds.

3. It was shown that esters of dialkylarsenious acids hydrolyze in the air with formation of the corresponding dialkylarsenious acids.

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INTERACTION OF DIALKYLPHOSPHOROUS ACIDS WITH ALDEHYDES AND KETONES

XX. ESTERS OF SOME α-HYDROXYALKYLTHIOPHOSPHONIC ACIDS

V. S. Abramov and V. K. Khairullin

Kazan Institute of Chemical Technology

Condensations of dialkylphosphorous acids with carbonyl compounds, the subject of our earlier work [1], are finding ever wider applications. It was recently shown that partial esters of aryl(alkyl)phosphonous acids [2] and dialkylphosphonous acids [3] react with aldehydes and ketones in the same manner as dialkyl phosphites; heterocyclic ketones [4] enter into reaction with dialkylphosphorous acids and form the corresponding esters of α--hydroxyalkylphosphonic acids, while thiourea gives esters of α-sulfhydryldiaminomethylphosphonic acid [5]. We should naturally expect thioanalogs of dialkyl phosphites and the like to react in the same way with aldehydes and ketones. Only isolated cases have been reported of the action of dialkyl thiophosphites on aldehydes and ketones [6]. This may be probably accounted for by the difficult accessibility of dialkyl thiophosphites which were prepared for the first time by the action of alcohols on phosphorus heptasulfide together with other thio derivatives of phosphorus. Yields were small [7]. It was shown only recently [8] that the action of hydrogen sulfide on halides of organic acids of pentavalent phosphorus in presence of tertiary bases leads to formation of thiopyro derivatives, while the same reaction applied to dialkyl chlorophosphites and their analogs leads to dialkylthiophosphorous acids in good yields.

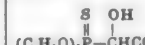
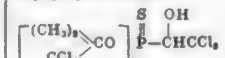
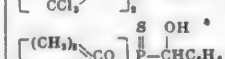
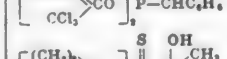
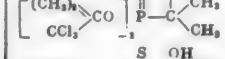
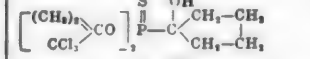
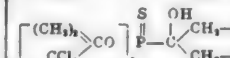
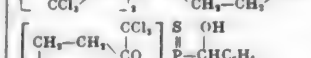
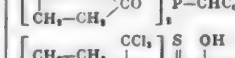
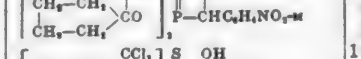
The dialkyl or diaryl thiophosphites needed for our investigation were obtained by the action of hydrogen sulfide on the corresponding acid chlorides. In the first experiments the reactions were performed in presence of pyridine. It appeared to us, however, that the reaction then went not only with formation of dialkyl thiophosphites but also of thiopyro derivatives.

$$(RO)_2PCl + H_2S + C_5H_5N \begin{cases} \nearrow (RO)_2PSH + C_5H_5N \cdot HCl \\ \searrow (RO)_2PSP(OR)_2 + C_5H_5N \cdot HCl \end{cases}$$

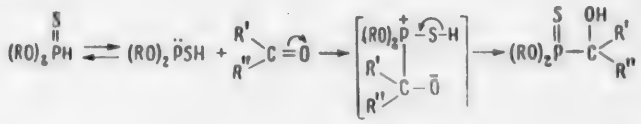
The pyro derivative, together with the resulting pyridine hydrochloride, although present in very minor quantity, mixes with the dialkyl thiophosphite and gives an impure product. In later experiments we therefore obtained dialkyl thiophosphites by direct action of hydrogen sulfide on acid chlorides and removed the hydrogen chloride with excess of hydrogen sulfide. The hydrogen sulfide and the solvent were removed from the dialkyl thiophosphites in vacuo. Thiophosphites are obtained more easily and in purer form by this method.

The dialkyl and diaryl thiophosphites were used in their crude form for condensations with aldehydes and ketones. Study of these reactions revealed that dialkyl thiophosphites add on at the >C = O bond of carbonyl compounds and give esters of α-hydroxyalkyl thiophosphonic acids in good yield. The reactions go at room temperature and are completed in several dozen hours. The addition products are most frequently obtained in the form of syrupy, viscous liquids or glassy masses. In course of time some of the syrupy products crystallized; they were then usually recrystallized from acetone which was found to be generally a good solvent for recrystallization of esters of α-hydroxyalkyl thiophosphonic acids. Only the crystalline esters can be obtained in the chemically pure form. Many of the syrupy and hard, vitreous products could not be purified since they did not crystallize, and they decomposed when their distillation was attempted. The prepared esters are presented in the table.

Esters of α-Hydroxyalkyl Thiophosphonic Acids

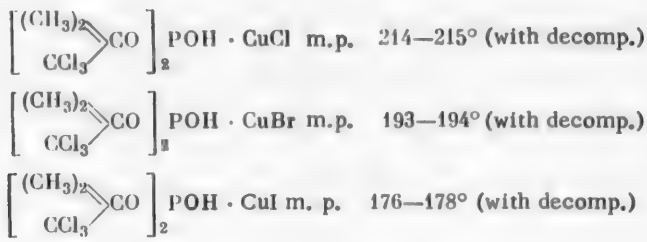
Preparation No.	Formula of prepared ester	Name of ester	Reaction period (hr)	M. p.	Yield (in %)	% Cl		% S		% P	
						found	calc.	found	calc.	found	calc.
1		Phenyl ester of α-hydroxy-(β,β,β-trichloro)-ethylthiophosphonic acid	—	124—126°	61.0	26.60	26.72	7.77	8.06	7.46	7.79
2		Tert-(1,1,1-trichloro)-butyl ester of α-hydroxy-(β,β,β-trichloro)-ethyl-thiophosphonic acid	19	181—182	55.0	56.25	56.54	5.40	5.68	5.31	5.49
3		Tert-(1,1,1-trichloro)-butyl ester of α-hydroxybenzyl thiophosphonic acid	48	167—168	85.0	40.41	40.67	5.95	6.13	5.81	5.93
4		Tert-(1,1,1-trichloro)-butyl ester of α-hydroxyisopropyl thiophosphonic acid	—	153—155	39.8	44.79	44.78	6.49	6.75	6.40	6.52
5		Tert-(1,1,1-trichloro)-butyl ester of α-hydroxycyclopentyl thiophosphonic acid	56	172—174	89.0	42.30	42.46	6.17	6.40	6.02	6.18
6		Tert-(1,1,1-trichloro)-butyl ester of α-hydroxycyclohexyl thiophosphonic acid	42	181—183	91.0	41.10	41.30	5.99	6.22	5.92	6.01
7		1-Trichloromethylcyclopentyl ester of α-hydroxybenzyl thiophosphonic acid	220	142—143	40.0	37.00	36.99	5.21	5.57	5.39	5.39
8		1-Trichloromethylcyclopentyl ester of α-hydroxy-m-nitrobenzyl thiophosphonic acid	15	157—158	57.5	34.11	34.30	5.07	5.17	4.63	5.00
9		1-Trichloromethylcyclopentyl ester of α-hydroxyisopropyl thiophosphonic acid	—	162—163	63.0	40.46	40.36	5.83	6.08	5.51	5.88
10		1-Trichloromethylcyclopentyl ester of α-hydroxycyclohexyl thiophosphonic acid	48	158—160	72.0	37.39	37.51	5.40	5.65	5.20	5.46

Formation of esters of α-hydroxyalkyl thiophosphonic acids can be represented as follows, by analogy with the reaction of dialkyl phosphites:

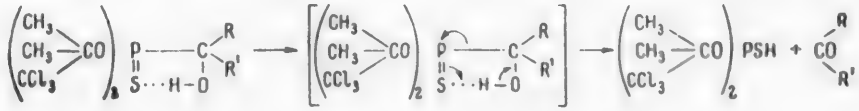


Like dialkyl phosphites [10], dialkylthiophosphites [9] are undoubtedly tautomeric. It must be assumed that the reaction goes with the enolic form of dialkyl thiophosphorus acid, the lone pair of electrons of the trivalent phosphorus of which reacts with the electronophilic carbon of the carbonyl group. It is known, however, that the tautomeric equilibrium of dialkyl thiophosphites is strongly shifted towards the keto-form containing pentavalent phosphorus [11]. The course of the reaction with carbonyl compounds is favored by the reaction of formation of esters of α-hydroxyalkyl thiophosphonic acids which gradually shifts the tautomeric equilibrium towards the side of the enolic form containing trivalent phosphorus. Moreover the presence of chlorine atoms in the radical of thioacids influences the state of equilibrium and evidently shifts it to the side of the enolic form to such an extent that their reaction with aldehydes and ketones becomes possible and goes to completion.

We showed previously [12] that ditert-(1, 1, 1-trichloro)-butyl phosphorous acid and like compounds add on to the carbonyl group of aldehydes and ketones in the absence of a catalyst at room temperature. We attributed the course of these reactions to partial shift of the tautomeric equilibrium towards the side of the enolic form containing trivalent phosphorus. This conclusion is confirmed by the exothermic reaction of diter-(1, 1, 1-trichloro)--butyl phosphorous acid with copper halides to give crystalline addition products which were recrystallized from a mixture of chloroform and methanol.



In contrast to the behavior of esters of alkylphosphonic acids, esters of α-hydroxyalkylphosphonic acids are easily cleaved at the P-C bond when heated with caustic alkalies. This is attributed to the presence of an intramolecular hydrogen bond [13, 3]. It was necessary to assume that esters of α-hydroxyalkylthiophosphonic acids have a similar susceptibility to cleavage at the P-C bond, although a hydrogen bond with sulfur is more rarely and more weakly developed [14].



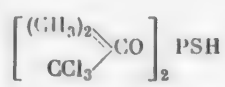
The esters do indeed decompose when heated to 180 – 200°, and the process is reflected in change of viscosity and in the development of the odor of the starting substances. The action of 1 N sodium hydroxide on the tert-(1, 1, 1-trichloro)-butyl ester of α-hydroxybenzyl thiophosphonic acid causes decomposition to start at 25 - 30° and to be completed at 50° with formation of the original components. Benzaldehyde was detected by odor.

EXPERIMENTAL

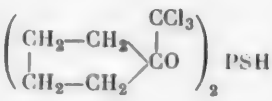
Preparation of dialkylthiophosphorous acids. Five-tenths mole acid chloride of dialkyl or diaryl phosphorous acid in 150 – 200 ml dry ether was placed in a round-bottomed flask. A stream of dry hydrogen sulfide was passed through a tube, extending into the solution, until hydrogen chloride could not longer be detected by

reaction with ammonia in the gases leaving the flask. The ether and excess of hydrogen sulfide were then removed in vacuo. The residue of dialkyl or diaryl thiophosphorous acid was usually a syrupy liquid which could not be distilled in vacuo and which broke down with release of sulfur. It was used in the crude form for reaction with aldehydes and ketones.

The following dialkyl thiophosphorous acids were prepared:



Ditert-(1, 1, 1-trichloro)-butyl thiophosphorous acid is a non-crystallizing, viscous, yellowish liquid; yield of crude product 94%.



Di-1-trichloromethylcyclopentyl-1-thiophosphorous acid, m.p. 80 – 82°, deliquescing in the air; yield of crude substance 96%.

$(C_6H_5O)_2PSH$

Diphenyl thiophosphorous acid is a viscous, colorless liquid; yield of crude product 98%.

Condensation of diphenylthiophosphorous acid with aldehydes and ketones. Reaction was conducted in ampoules in which 4.6 g diphenyl thiophosphorous acid and an equimolar quantity of the aldehyde or ketone were sealed. The mixture was left at room temperature. After a few days the viscosity of the reaction mixture increased appreciably, indicating that condensation had occurred. The product of condensation with chloral was converted into a crystalline mass from which the diphenyl ester of α-hydroxy-β, β, β-trichloroethyl thiophosphorous acid was isolated (see table). Uncrystallizable liquids with an unpleasant odor were obtained in reactions of diphenyl thiophosphorous acid with acetaldehyde, propionaldehyde, butyraldehyde and isovaleraldehyde; similarly with benzaldehyde, o-, m- and p-nitrobenzaldehydes, acetone, cyclopentanone, cyclohexanone and chloroacetone. Salicylaldehyde reacts with considerable release of heat and forms a carmine-colored vitreous mass.

Condensation of ditert-(chlorosubstituted)-alkyl thiophosphorous acids with aldehydes and ketones. Dialkyl thiophosphorus acids (0.01 mole and anequimolar quantity of aldehyde or ketone were sealed into ampoules which were left at room temperature. After a few days the reaction mixtures became much more viscous and some of them had changed into crystalline masses. The crystalline esters of α-hydroxyalkyl thiophosphonic acids were recrystallized from acetone. White, well-formed, crystals were obtained. Some of the esters had a faint garlic-like odor. The esters were insoluble in water and poorly soluble in common organic solvents. The prepared esters are listed in the table.

The products of reaction of ditert-(1, 1, 1-trichloro)-butyl thiophosphorous acid with acetaldehyde, propionaldehyde, butyraldehyde and isovaleraldehyde, also with p- and m-nitrobenzaldehydes, chloroacetone, etc., were obtained in the form of viscous, syrupy liquids which did not crystallize after prolonged standing so that the esters could not be obtained in the chemically pure form.

The products of reaction of di-1-trichloromethylcyclopentyl-1-phosphorous acid with acetaldehyde, propionaldehyde, butyraldehyde, isovaleraldehyde, etc., were likewise obtained only in the form of noncrystallizing syrups. Salicylaldehyde reacts with both of the dialkyl thiophosphorous acids with considerable release of heat and forms a vitreous, hard carmine-colored mass.

Condensations were effected in the absence of catalyst. Preliminary experiments established that the reaction is not appreciably catalyzed by sodium ethoxide and triethylamine.

Action of caustic alkali on esters of α-hydroxyalkyl thiophosphonic acids. 0.5 g tert-(1, 1, 1-trichloro)--butyl ester of α-hydroxybenzyl thiophosphonic acid was put in a test tube and 1 ml of 1 N alkali solution was run in. A weak odor of benzaldehyde was developed at 25 – 30°, and at 50° the ester had been completely decomposed into benzaldehyde and thioacid, both of which were detected by their characteristic odors.

SUMMARY

1. Dialkyl thiophosphorous acids can be obtained by the direct action of hydrogen sulfide on dialkyl chlorophosphites in good yield.

2. Dialkyl thiophosphorous acids undergo condensations with aldehydes and ketones to form esters of α--hydroxyalkyl thiophosphonic acids. Ten esters of α-hydroxyalkyl thiophosphonic acids were synthesized.

3. Aldehydes and ketones condense with the enolic form of the thioacid. The shift of the tautomeric equilibrium toward the side of the enolic form is favored by formation of esters of α-hydroxyalkyl thiophosphonic acids and by the presence of chlorine at the thioacid radicals.

4. Esters of α-hydroxyalkyl thiophosphonic acids are easily cleaved at the P-C bond when warmed with caustic alkali. This may be due to the presence of a hydrogen bond.

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EFFECT OF STRUCTURE OF OLEFINS ON THEIR ACTIVITY IN CHAIN TRANSFER DURING POLYMERIZATION

A. P. Titov and I. A. Livshits

S. V. Lebedev All-Union Synthetic Rubber Research Institute

In studying the effect of ethylenic hydrocarbons on the polymerization of butadiene with sodium metal it was shown by one of us [1] that when butadiene is polymerized in admixture with 2-butene, 2-pentene or 2-hexene, the molecular weight of the polymers decreases as the molecular weight of the ethylenic hydrocarbon decreases. Further studies in this direction [2] revealed that the same rule also holds when butadiene is polymerized in media of monosubstituted ethylenic hydrocarbons with a straight-chain structure. In the case of ethylenic hydrocarbons with an iso structure it was shown that the higher the dipole moment of the olefin, the lower the molecular weight of the polybutadiene. These phenomena were explained on the basis that olefins participate in chain transfer, chiefly through cleavage of the hydrogen atoms attached to the α-carbon atom (relative to the double bond).

It seemed of interest also to study the effect of the indicated olefins in other types of polymerization, and particularly in radical polymerization. The fragmentary information existing on the reactivity of olefins in radical polymerization deals with studying the acts of chain growth, and actual data on the participation of olefins in chain transfer are lacking.

To study the relationship between olefin structure and its activity in chain transfer during radical polymerization, we ran experiments on the thermal polymerization of styrene in which 16 olefins of variable structure were used as solvent. Based on literature data, it is possible to assume that when olefins are copolymerized with styrene, giving a free radical of low activity during polymerization, they will be present in the composition of the copolymer only in small amount. In connection with this we deemed it possible to consider the polymerization of a mixture of styrene and ethylenic hydrocarbon to be the same as the polymerization of styrene in a solution of chain transfer agent, in this case the olefin.

Using Mayo's formula [3], we calculated the values of the chain transfer constant K, characterizing the relative activity of different olefins in this reaction.

Assuming the additivity principle to apply, we calculated for each alkene the fraction of the total value of the transfer constant falling to one active (attached to the α-carbon atom with respect to the double bond) hydrogen atom, attached to a primary, secondary and tertiary carbon atom, respectively. Such a calculation method is approximate, but can be useful for establishing some qualitative rules. An examination of the results obtained by us (Table 1) permits concluding that the activity of olefinic hydrocarbons in the chain transfer reaction is definitely related to their structure. Comparison of the effect shown by olefins, containing primary – (I), (III), (V), (XI), secondary – (II), (IV), (VI), (VII), (IX) and tertiary – (VIII), (X) carbon atoms, reveals that the mobility of the hydrogen atoms attached to α-carbon atoms (with respect to the double bond) is least for primary, greater for secondary, and greatest for tertiary carbon atoms. With increase in the number of substitutents on the carbon atoms found attached to the double bond, the activity in the chain transfer reaction increases, both for the olefin molecule as a whole and for the individual hydrogen atoms, attached to α-carbon atoms – (I), (III), (XI).

The activity of olefins changes depending on the location of the substituents of the carbon atoms attached to the double bond. When the substituents in the olefin molecule are located on different sides of the double bond, the activity of the olefin is somewhat greater than where the substitutents are on the same side of the double bond. This is seen when the fraction of K, falling to one active hydrogen atom, for the hydrogen on the primary α-carbon atom in olefins (I) and (V) is compared with that for the hydrogen found on the secondary α-carbon atom

TABLE 1

No. of compound	Compound	Transfer constant $K \cdot 10^4$	Fraction of K falling to one active hydrogen atom, found on α-carbon atom		
			primary	secondary	tertiary
(I)	2-Methyl-1-propene	1.7	0.28	—	—
(II)	2-Methyl-1-butene	3.1	0.28	1.13	—
(III)	2-Methyl-2-butene	2.9	0.32	—	—
(IV)	2-Methyl-2-pentene	6.3	0.32	2.19	—
(V)	2-Butene	2.0	0.33	—	—
(VI)	2-Pentene	4.2	0.33	1.6	—
(VII)	1-Pentene	2.3	—	1.15	—
(VIII)	3-Methyl-1-butene	6.9	—	—	6.9
(IX)	2-Hexene	3.6	0.33	1.30	—
(X)	4-Methyl-2-pentene	6.9	0.33	—	5.9
(XI)	2,3-Dimethyl-2-butene	5.4	0.45	—	—

TABLE 2

Hydrocarbon	Transfer constant $K \cdot 10^4$
Hexane	0.9
1-Butene	2.6
1-Pentene	2.3
1-Hexene	2.5
1-Heptene	2.7
2-Pentene	4.2
2-Hexene	3.6
2-Heptene	3.2
2-Octene	2.8

in olefins (II) and (VI). Change in activity as a function of the chain length of the molecule is not the same for 1- and 2-alkenes. In the case of n-1-alkenes the activity is not affected by the chain length; in the case of n-2-alkenes there is a tendency for the activity to decrease as the molecular weight of the olefin increases (Table 2). All of the olefins studied by us are more active in the chain transfer reaction than are the straight-chain saturated hydrocarbons (Table 2).

The rules obtained by us show good agreement with the literature data on the reactivity of olefins in radical processes. Thus, a difference in the reactivity of hydrogen atoms, linked to primary, secondary and tertiary α-carbon atoms (with respect to the double bond), is known for the oxidation of olefins [4, 5], the reactions

TABLE 3

Constants of Starting Hydrocarbons

Hydrocarbon	Boiling point	d_4^{20}	n_D^{20}
Styrene	50° (24 mm)	0.9075	1.5470
Hexane	68.5–68.8	0.6592	1.3745
1-Butene	– 6.3	–	–
2-Butene	1.0– 1.3	–	–
2-Methylpropene	– 6.9	–	–
1-Pentene	30.0–30.3	0.6404	1.3713
1-Hexene	63.4–63.8	0.6735	1.3885
1-Heptene	93.4–93.8	0.6969	1.3997
2-Methyl-2-butene	38.0–38.5	0.6616	1.3870
2-Methyl-2-pentene	67.0–67.5	0.6857	1.4000
2, 3-Dimethyl-2-butene	73.0–73.5	0.7075	1.4120
2-Methyl-1-butene	31.0	0.6501	1.3780
3-Methyl-1-butene	20.5	0.6270	1.3640
4-Methyl-2-pentene (mixture of cis and trans)	58.0–59.0	0.6670 •	1.3885
2-Pentene (mixture of cis and trans)	36.0–36.5	0.6485	1.3795
2-Hexene (mixture of cis and trans)	67.8–68.2	0.6795	1.3949
2-Heptene (mixture of cis and trans)	97.8–98.3	0.7040	1.4060
2-Octene (mixture of cis and trans)	124.8–125.3	0.7200	1.4135

• At 25°.

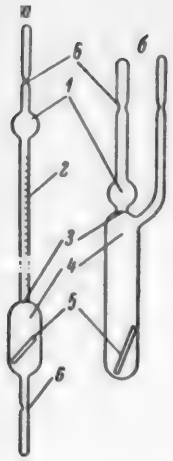

Fig. 1. Reaction ampules. 1) 4 ml bulb for adding styrene in doses, 2) graduated portion for following rate of polymerization, 3) partition, broken prior to start of experiment, 4) small cylinder for adding solvent in doses, 5) hammer for breaking partition, 6) constrictions for sealing off ampule.

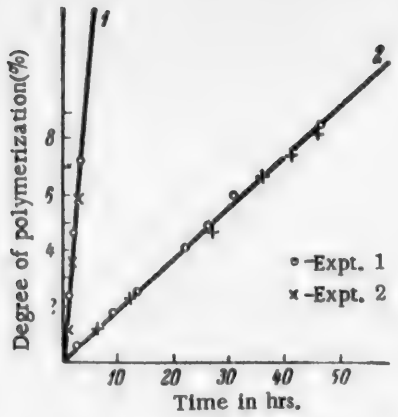

Fig. 2. Polymerization rate of styrene. 1) Styrene without solvent, 2) styrene in hexane solution. Styrene: hexane mole ratio = 1:3

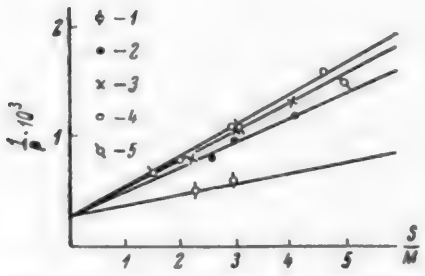

Fig. 3. Graphical determination of transfer constant for 1-alkenes. 1) hexane, 2) 1-pentene, 3) 1-hexene, 4) 1-heptene, 5) 1-butene

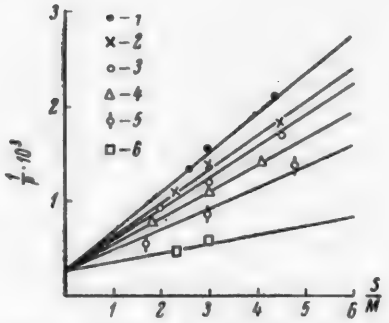

Fig. 4. Graphical determination of transfer constant for 2-alkenes. 1) 2-pentene, 2) 2-hexane, 3) 2-heptene, 4) 2-octene, 5) 2-butene, 6) hexane

of olefins with free methyl radicals [6], and for other reactions. The same type of rule was also found by a number of authors [7 – 9] for the radical polymerization of styrene and other monomers in solutions of benzene derivatives.

The effect of the number of substituents found at the double bond on olefin activity was also observed by Trotman-Dickenson and Steacie [6] for the case of cleaving hydrogen atoms, found on α-carbon atoms, with free methyl radicals.

The effect exerted by the location of substitutents in the olefin molecule on its activity in reactions involving replacement of hydrogen atoms is in agreement with the results obtained in some recent studies by B. A. Dolgoplosk and co-workers [10]. In these studies it was shown that the ability of free radicals to add to olefin double bonds decreases, and the ability to cleave hydrogen atoms increases, when the double bond is shifted from the 1 to the 2 position.

A comparison of the results obtained by us in the thermopolymerization of styrene in the presence of ethylenic hydrocarbons with the results obtained by us earlier in the polymerization of butadiene with sodium in the

TABLE 4

Polymerization of Styrene in Solutions of Iso Olefins at 100°

Solvent	Styrene concentration (in moles)	Time (in hr)	Degree of polymerization (in %)	Average polymerization rate $\left(\frac{\text{mole}}{\text{liter/sec}} \cdot 10^6\right)$	Molecular weight of polymer (in thousands)
2-Methyl-1-propene	2.68	20.6	6.0	2.2	172
	2.16	20.6	5.0	1.5	115
	1.56	66.0	7.1	0.5	91
2-Methyl-2-butene	3.04	19.5	10.8	4.7	130
	2.05	30.5	9.0	1.7	98
	1.22	173.3	20.9	0.4	49
2-Methyl-1-butene	2.59	30.5	12.7	3.0	115
	1.48	119.0	17.8	0.6	56
	1.16	173.3	15.9	0.3	49
2,3-Dimethyl-2-butene	3.16	19.5	10.2	4.6	98
	2.31	23.5	10.0	2.7	70
	1.23	119.0	19.5	0.6	35
2-Methyl-2-pentene	2.92	19.5	8.7	3.6	87
	1.98	59.0	17.0	1.6	48
	1.17	173.3	21.0	0.4	28
3-Methyl-1-butene	3.2	19.5	10.7	4.9	79
	2.41	30.5	8.0	1.76	54
	1.33	161.8	14.5	0.3	29
4-Methyl-2-pentene	1.98	30.5	9.0	1.6	48
	1.42	120.0	15.0	0.5	33

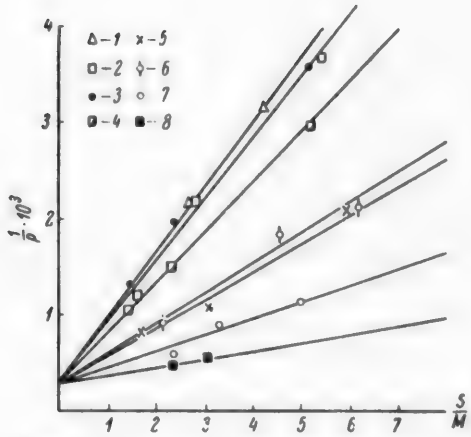

Fig. 5. Graphical determination of transfer constant for iso olefins. 1) 4-methyl-2-pentene, 2) 2-methyl-2-pentene, 3) 3-methyl-1-butene, 4) 2, 3-dimethyl-2-butene, 5) 2-methyl-2-butene, 6) 2-methyl-1-butene, 7) 2-methylpropene, 8) hexane

presence of the same hydrocarbons [1, 2], reveals that in the chain transfer reaction the character of change in the activity as a function of olefin structure is different for each type of polymerization.

EXPERIMENTAL

Starting Products

Styrene (99.8 – 100%) was obtained by the dehydration of ethylbenzene. Its purity was judged by the absence of an induction period when polymerized. 1-Butene and 2-butene were isolated from the technical butylene of SR plants by careful fractional distillation, and were purified from isobutylene by washing with sulfuric acid. Isobutylene was obtained by the dehydration of trimethylcarbinol over oxalic acid. 1-Pentene, 1-hexene and 1-heptene were synthesized from allyl chloride and the proper bromides [11]. 2-Pentene, 2-hexene, 4-methyl-2-pentene and 2, 3-dimethyl-2-butene were obtained by dehydration of the corresponding alcohols with sulfuric acid, while 2-methyl-2-butene and 2-methyl-2-pentene were obtained by dehydration of corresponding alcohols over oxalic acid [12, 13]. 3-Methyl-1-butene and 2-methyl-1-butene were obtained by the dehydration of isoamyl alcohol over aluminum oxide [14], with subsequent careful fractional distillation of the reaction mixture. 2-Heptene and 2-octene were synthesized by the Grignard reaction from divinyl hydrobromide and the proper alkyl bromides [15, 16].

TABLE 5

Polymerization of Styrene in Solutions of Normal Olefins at 100°

Solvent	Styrene concentration (in moles)	Time (in hr)	Degree of polymerization (in %)	Average polymerization rate ($\frac{\text{mole}}{\text{liter/sec}} \cdot 10^6$)	Molecular weight of polymer (in thousands)
Without solvent	8.09	3.0	7.2	53.9	380
Hexane	2.19	30	8.65	1.75	222
	1.79	47	8.4	0.9	180
1-Butene	3.56	9.5	7.0	7.3	160
	2.30	30	7.0	1.5	94
	1.55	48	8.0	0.7	70
	2.29	30	9.2	2.0	127
1-Pentene	2.04	30	7.5	1.4	106
	1.61	53	9.0	0.8	86
	2.29	30	10.8	2.3	132
1-Hexene	1.83	30	8.6	1.5	96
	1.46	53	8.8	0.7	82
	2.28	30	11.9	2.5	134
1-Heptene	1.69	30	8.1	1.3	95
	1.18	53	7.5	0.5	65
	3.32	7.7	6.0	7.2	190
2-Butene	2.30	30.0	7.1	1.5	118
	1.61	46.7	8.5	0.8	77
	2.26	30	10.5	2.2	77
2-Pentene	2.06	30	8.8	1.7	68
	1.53	53	9.3	0.7	49
	2.28	30	11.8	2.5	96
2-Hexene	1.86	30	10.0	1.7	76
	1.34	53	9.3	0.7	57
	2.29	30	12.6	2.6	108
2-Heptene	1.69	30	9.0	1.4	87
	1.21	53	9.7	0.6	61
	2.28	30	12.9	2.7	126
2-Octene	1.55	30	9.6	1.4	96
	1.20	53	9.5	0.6	74

The olefins obtained in this manner were kept for a long time over sodium wire at 70°, and then fractionated through a laboratory column with an efficiency of 50 theoretical plates. The constants of the starting hydrocarbons are given in Table 3.

Apparatus and Mode of Operation

Polymerization was run in glass ampuls (Fig. 1), composed of two parts, separated by a partition. Adding the styrene and solvents in doses was effected by vacuum-distillation into test tubes, from which the air had previously been displaced with nitrogen. The solvents were first kept over butyllithium for 2 – 3 hours. The experiments were run at 100 ± 0.2°. The rate of polymerization was followed by the decrease in the volume of the polymerization mixture. The final degree of polymerization was calculated on the weight of polymer. In all

cases the polymerization was terminated when it had gone 10 – 20%. The reaction ampuls with the graduated portion (Fig. 1, a) were used to run the experiments on the polymerization of styrene in solutions of normal olefins at a molar ratio of 1:3. In these experiments a good reproducibility of the polymerization rate was obtained in parallel experiments. To simplify the work with the other ratios of styrene to n-olefin, and also when styrene was polymerized in solutions of n-butylenes and olefins of iso structure, the experiments were run in ampuls minus the graduated portion (Fig. 1, b).

The molecular weight of the polymer was calculated using the equation given in [17]: $M = 167{,}000 \cdot [\eta]^{1.37}$.

The intrinsic viscosity (η) of the polymer was found by graphical extrapolation of the viscosity values for four different concentrations of the polymer in benzene solution to zero concentration.

The relative viscosity of the polymer solutions was determined using an Ostwald viscosimeter.

The transfer constant was determined graphically by solving Mayo's equation [3]:

$$\frac{1}{P} = \frac{1}{P_0} + K\frac{S}{M},$$

where P is the degree of styrene polymerization in solution of chain-transfer agent, P_0 is the degree of styrene polymerization without solvent, S is the number of moles of solvent, M is the number of moles of styrene, and K is the transfer constant, characterizing the relative activity of the solvent in the chain transfer reaction.

Results Obtained

We determined the initial rates for the thermal polymerization of styrene and the molecular weight values of the polymers both for the polymerization of styrene alone and for its polymerization in n-hexane solution and in 16 olefins of different structure with variation in the styrene concentration. The results of these experiments are given in Tables 4 and 5.

The rates for the polymerization of styrene alone and for its polymerization in hexane solution are shown in Fig. 2. A similar agreement of the results in parallel experiments was also observed when styrene was polymerized in olefin solution. Figs. 3 – 5 illustrate the graphical determination of the chain transfer constant for the polymerization of styrene in solutions of the hydrocarbons investigated by us.

SUMMARY

1. The thermal polymerization of styrene in hexane solution and in solutions of 16 olefins with variable structure was studied.

2. It was shown that the activity of olefins, as chain transfer agents, increases when: a) transition is from olefins containing primary carbon atoms in the α-position to the double bond to olefins containing secondary carbon atoms in the α-position and, to an even greater degree, when transition is to olefins with tertiary α-carbon atoms; b) the number of substitutents on the carbon atoms attached to the double bond is increased; and c) substituents are shifted from the position of being on the same side of the double bond to that of being on opposite sides.

3. It was shown that the relationship between the activity of olefins in the chain transfer reaction and their structure is dependent on the type of polymerization involved.

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ORGANIC INSECTOFUNGICIDES

XLII. SYNTHESIS OF SOME MIXED ESTERS OF DITHIOPHOSPHORIC ACID

N. N. Mel'nikov, K. D. Shevtsova-Shilovskaya, M. Ya. Kazan and I. M. Mil'shtein

Research Institute on Fertilizers and Insectofungicides

In recent years, in connection with the discovery of insecticidal properties for various esters and other derivatives of phosphoric, thiophosphoric and dithiophosphoric acid, intensive research is being conducted on the synthesis and study of a large number of new organic phosphorus compounds. The compounds described in the literature up to now are characterized by a broad diversity [1-10]. However, nearly all of the mixed aliphatic-aromatic esters of dithiophosphoric acid described in the literature have the aromatic radicals connected directly to the phosphoric acid radical through the aromatic ring, whereas the number of mixed esters of dithiophosphoric acid in which the aromatic radical is separated from the dithiophosphoric acid portion of the molecule by one or more CH_2 groups can be counted singly [10, 11].

In connection with a study on the manner in which organophosphorus insecticides act on insects, and to establish the nature of the relationship existing between structure and insecticidal activity in this series of compounds, it seemed appropriate to synthesize some mixed esters of thiophosphoric acid and of dithiophosphoric acid with general formula (I)-(IV).

$$\underset{\text{(I)}}{(RO)_2PSS(CH_2)_nAr} \qquad \underset{\text{(II)}\quad X = OS}{(RO)_2PSS(CH_2)_nXAr}$$

$$\underset{\text{(III)}}{(RO)_2PSS(CH_2)_nNR'_2} \qquad \underset{\text{(IV)}}{(RO)_2PSO(CH_2)_nAr}$$

First, we synthesized the mixed esters of thiophosphoric acid with general formula (I) and (II). These compounds were synthesized by reacting the salts of dialkyldithiophosphoric acids with the proper halo derivatives, according to the schemes

$$(RO)_2PSSK + Cl(CH_2)_nAr \longrightarrow (RO)_2PSS(CH_2)_nAr + KCl$$

$$(RO)_2PSSK + ClCH_2CH_2OAr \longrightarrow (RO)_2PSSCH_2CH_2OAr + KCl$$

It should be mentioned that in some cases the reaction between the salts of dialkyldithiophosphoric acids and the halo derivatives goes very slowly, and the corresponding esters are obtained in extremely low yields. Reaction is especially bad in the case of the salts of dimethyldithiophosphoric acid, which in many cases behave abnormally; this, apparently, is linked with the relatively great mobility of the methyl radical, as a result of which the methyl esters of phosphorus acids function as alkylating (methylation) agents. Also, according to Pishchimuka [12], the methyl esters isomerize much more easily.

The mixed esters of dithiophosphoric acid synthesized by us, and their properties, are given in the table. Nearly all the compounds given in the table are new; the only exceptions are the esters with the p-chlorobenzyl radical, which were recently pantented by G. Schrader [11] for use as insecticides.

EXPERIMENTAL

Preparation of O,O-dialkyl-S-benzyldithiophosphates. These compounds were synthesized as follows. The potassium dialkyldithiophosphate and proper solvent (as solvent we used either acetone or an alcohol; the alcohol used had the same structure as that used to prepare the dialkyldithiophosphoric acid) were placed in a flask fitted with reflux condenser, mechanical stirrer and dropping funnel, and then an equimolar amount of the proper benzyl chloride derivative was added gradually from the dropping funnel. When all of the benzyl chloride derivative (or 1-aryl-3-bromopropane) had been added, the reaction mixture was stirred under reflux for not less than 2.5-3 hours. The reaction mixture after cooling was diluted with benzene; the benzene solution was washed several times with water, then dried over anhydrous sodium sulfate, the solvent distilled off, and the residue fractionally distilled in vacuo. It should be mentioned that to obtain some of the compounds analytically pure it proved necessary to fractionally distill under a high vacuum 2-3 times. O,O-Dimethyl-S-4-nitrobenzyldithiophosphate and O,O-diisopropyl-S-4-nitrobenzyldithiophosphate could not be distilled even under a high vacuum, and these compounds were obtained quite impure.

The O,O-dialkyl-S-2-phenoxyethyldithiophosphates were prepared in exactly the same manner; here reaction went much slower, and consequently the reaction mixture had to be heated for at least 6-8 hours. The compounds obtained by us, and their properties, are given in the table.

Formula	Yield (in %)	B. p. (pressure in mm)	d_4^{20}	n_D^{20}	% P	
					found	calc.
$(CH_3O)_2PSSCH_2C_6H_5$	53	117—117.5° (0.11)	1.2217	1.5818	11.73	12.47
$(C_2H_5O)_2PSSCH_2C_6H_5$	50	112—112.5 (0.07)	1.1571	1.5600	11.09	11.22
$(C_3H_7O)_2PSSCH_2C_6H_5$	80	132—133 (0.12)	1.1105	1.5461	9.89	10.18
iso-$(C_3H_7O)_2PSSCH_2C_6H_5$	66	118—120 (0.12)	1.1103	1.5432	10.25	10.18
$(C_4H_9O)_2PSSCH_2C_6H_5$	77	136—138 (0.1)	1.0849	1.539	9.25	9.32
$(CH_3O)_2PSSCH_2C_6H_4Cl$ [m]	42	133—135 (0.16)	1.3046	1.5897	10.31	10.95
$(C_2H_5O)_2PSSCH_2C_6H_4Cl$ [m]	60	138—140 (0.35)	1.2278	1.5675	10.19	9.97
$(C_3H_7O)_2PSSCH_2C_6H_4Cl$ [m]	63	137—138 (0.1)	1.1739	1.5560	8.90	9.14
iso-$(C_3H_7O)_2PSSCH_2C_6H_4Cl$ [m]	53	138.5—140 (0.2)	1.1745	1.5518	9.48	9.14
$(C_4H_9O)_2PSSCH_2C_6H_4Cl$	61	154—155 (0.09)	1.1378	1.5460	8.51	8.44
$(CH_3O)_2PSSCH_2C_6H_4NO_2$	71	Decomposes when distilled	—	—	—	—
$(C_2H_5O)_2PSSCH_2C_6H_4NO_2$	47	168—174 (0.1)	1.2807	1.5775	9.42	9.65
iso-$(C_3H_7O)_2PSSCH_2C_6H_4NO_2$	79	Decomposes when distilled	—	—	—	—
$(CH_3O)_2PSSCH_2CH_2CH_2C_6H_5$	25	139—140 (0.1)	1.1712	1.5644	10.20	11.22
$(C_2H_5O)_2PSS(CH_2)_3C_6H_5$	40	140—142 (0.1)	1.1240	1.5472	9.81	10.17
mac-$(C_3H_7O)_2PSS(CH_2)_3C_6H_5$	60	149—151 (0.2)	1.0817	1.5332	9.19	9.31
$(CH_3O)_2PSS(CH_2)_2OC_6H_5$ *	18	140—142 (0.28)	1.2406	1.5698	—	—
$(C_2H_5O)_2PSS(CH_2)_2OC_6H_5$ **	41	132—134 (0.015)	1.1819	1.5525	10.24	10.11
$(C_3H_7O)_2PSS(CH_2)_2OC_6H_5$	58	145—146 (0.12)	1.1394	1.5418	8.84	9.25
iso-$(C_3H_7O)_2PSS(CH_2)_2OC_6H_5$ ***	59	144—145 (0.3)	1.1264	1.5365	8.85	9.25
$(C_4H_9O)_2PSS(CH_2)_2OC_6H_5$ ****	50	160—162 (0.12)	1.100	1.5339	8.34	8.54

SUMMARY

To study the mechanism of action and the dependence of insecticidal activity of mixed esters of dithiophosphoric acid on their structure, we synthesized a number of unknown compounds with general formula $(RO)_2PSS(CH_2)_nAr$ and $(RO_2)PSS(CH_2)_nOAr$. All of the mixed esters of dithiophosphoric acid were synthesized by reacting potassium dialkyldithiophosphates with the proper halo derivatives.

* Found %: C 43.78; H 5.07. Calculated %: C 43.17; H 5.07.

** Found %: C 46.33; H 6.55. Calculated %: C 47.04; H 6.25.

*** Found %: C 50.70; H 7.25. Calculated %: C 50.02; H 6.92.

**** Found %: C 55.56; H 7.63. Calculated %: C 53.01; H 7.50.

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ISOTOPIC EXCHANGE REACTION OF ARYLMERCURY CHLORIDES WITH METALLIC MERCURY, TAGGED WITH Hg^{203}

O. A. Reutov and G. M. Ostapchuk

Moscow State University

We had shown previously [1] that symmetrical organomercury compounds in the aromatic series show isotopic exchange with metallic mercury, tagged with Hg^{203}, under mild conditions.

$$(n\text{-}XC_6H_4)_2Hg + Hg \rightleftarrows (n\text{-}XC_6H_4)_2\overset{*}{Hg} + Hg$$

Depending on the nature of substituent X, the reaction rate increases in the following order: O_2N < $COOC_2H_5$ < Cl < H < CH_3 < OCH_3.

In this paper we discuss the results of studying the isotopic exchange of arylmercury chlorides with metallic mercury, tagged with Hg^{203}.

$$n\text{-}XC_6H_4\text{—}HgCl + \overset{*}{Hg} \rightleftarrows n\text{-}XC_6H_4\text{—}\overset{*}{Hg}Cl + Hg$$

All of the experiments were run under the same conditions. Into a three-necked 100-ml flask, fitted with stirrer and reflux condenser, were charged 50 ml of arylmercury chloride solution in anhydrous pyridine and metallic mercury, tagged with Hg^{203} (in all cases ~0.028 mole of arylmercury chloride and 1.4 moles of metallic mercury). The flask was placed in a thermostat, and the reaction was run at 60.0° ± 0.1° with stirring at a rate of 1500 ± 200 rpm. Samples (6 ml) were removed from the reaction mixture at periodic intervals. The colloidal mercury metal was removed from the sample by centrifuging, while the arylmercury chloride was precipitated with water containing hydrochloric acid. The precipitate was filtered, washed with water, and recrystallized from suitable solvent. The weighed substance was dissolved in organic solvent, the solution poured in drops on a standard filter, and the thin layer of substance obtained in this manner on the filter was coated with plexiglas lacquer. The radioactivity was measured using an MS-4 counter. The results of the experiments are summarized in the table.

From the data given in the table it follows that the rate of the discussed isotopic exchange reaction, as a function of the nature of substituent X, increases in the order: O_2N < C_2H_5OCO < Cl < H, CH_3.

As a result, the dependence of the rate of isotopic exchange for the cases of $(p\text{-}XC_6H_4)_2Hg$ and $P\text{-}XC_6H_4$ – HgCl with metallic mercury on the nature of substituent X bears a similar character, which is evidence that the mechanism is the same for both reactions.

It should be mentioned that all of the arylmercury chlorides react with metallic mercury more rapidly than do the corresponding diaryl organomercury compounds.

The discussed reaction is apparently homolytic, but not free-radical, since in contrast to diarylmercury compounds the arylmercury chlorides do not form free radicals even when their solutions are irradiated with ultraviolet light.

Results of Isotopic Exchange of Arylmercury Chlorides with Mercury in Pyridine*

Expt. No.	Arylmercury chloride	Reaction time (in hr)	No. of impulses observed (in min)	Equilibrium activity	Percent exchange
1	C_6H_5—HgCl	0.5	35	132	27
		1.0	104	132	79
		2.5	590	644	92
		3.5	572	587	98
2	C_6H_5—HgCl	0.5	90	296	30
		0.75	124	228	54
		1.0	193	296	65
		1.5	366	450	81
		2.5	528	565	94
		3.5	301	319	94
3	C_6H_5—HgCl	0.75	131	213	62
		1.0	241	347	70
		1.5	375	422	89
		2.5	166	160	100
		3.5	394	417	95
4	p-$CH_3C_6H_4$—HgCl	0.25	101	468	22
		0.5	227	727	31
		0.75	428	734	58
		1.0	68	94	72
		1.5	641	727	88
		2.0	694	720	96
5	p-$CH_3C_6H_4$—HgCl	0.25	120	468	26
		0.50	45	152	30
		0.75	293	483	61
		1.0	354	460	77
		1.95	387	460	84
		2.0	271	313	87
		2.5	459	460	100
		3.0	485	460	103
6	p-$CH_3C_6H_4$—HgCl	0.25	219	958	23
		0.5	469	1150	41
		1.0	623	948	66
		1.5	907	1136	80
		2.0	963	1115	86
		2.5	1023	1125	91
		3.0	1086	1160	94
7	p-ClC_6H_4—HgCl	0.5	31	154	20
		1.0	94	189	50
		1.5	133	217	61
		2.0	137	200	69
		2.5	256	343	75
		3.0	301	349	86
		4.0	77	86	90
		6.0	124	143	87
8	p-ClC_6H_4—HgCl	0.5	81	333	25
		0.75	110	323	35
		1.5	262	472	56
		2.0	330	508	66
		2.5	398	534	77
		3.0	396	508	78

* Phenylmercury chloride and p-chlorophenylmercury chloride were recrystallized from methyl alcohol, while the other arylmercury chlorides were recrystallized from acetone. For dropping on the filter, p-tolylmercury chloride was dissolved in chloroform, while the other arylmercury chlorides were dissolved in acetone. For all of the arylmercury chlorides, with the exception of p-carbethoxyphenylmercury chloride, the results of three parallel experiments are given.

Continued

Expt. No.	Arylmercury chloride	Reaction time (in hr)	No. of impulses observed (in min)	Equilibrium activity	Percent exchange
9	p-ClC_6H_4—HgCl	2.0	404	603	67
		6.0	323	383	84
		7.5	295	335	88
		10.5	822	977	84
10	p-$C_2H_5OCOC_6H_4$—HgCl	1.0	70	422	16
		3.0	237	510	47
		5.0	387	598	65
		7.0	381	520	73
		10.0	435	500	87
		14.0	451	506	89
		20.0	477	520	91
		25.0	466	506	92
11	p-$O_2NC_6H_4$—HgCl	1.0	18	467	4
		2.5	12	117	10
		4.0	88	331	27
		6.0	119	357	33
		8.0	200	409	49
12	p-$O_2NC_6H_4$—HgCl	4.0	138	440	32
		8.0	221	438	51
		12.0	255	417	61
		16.0	284	417	68
		20.0	301	438	69
13	p-$O_2NC_6H_4$—HgCl	8.0	315	565	56
		12.0	380	617	62
		16.0	387	564	69
		20.0	352	552	64
		24.0	453	587	77
		28.0	126	180	70
		32.0	386	525	74

It seems most probable to us that the reaction goes through the stage of forming a four-membered activated complex.*

$$Ar-Hg-Cl + \overset{*}{Hg} \rightleftharpoons \left[Ar\begin{matrix}\diagup Hg \diagdown Cl \\ \diagdown \overset{*}{Hg} \diagup\end{matrix}\right] \rightleftharpoons Ar-\overset{*}{Hg}-Cl + Hg$$

The possible alternate mechanisms:

and

(a) $R-Hg-Cl + \dot{H}g \rightleftharpoons R-Hg-\dot{H}g-Cl \rightleftharpoons R-\dot{H}g-Cl + Hg$

(b) $R-Hg-R + \dot{H}g \rightleftharpoons R-\dot{H}g-Hg-R \rightleftharpoons R-\dot{H}g-R + Hg$

seem less probable to us, although sufficient information is lacking at present to conclusively establish the mechanism of the reaction.

SUMMARY

1. The isotopic exchange of arylmercury chlorides with metallic mercury, tagged with radioactive isotope Hg^{203}, was studied.

* It has been postulated that the formation of a four-membered activated complex when symmetrical organomercury compounds are reacted with mercuric chloride is possible [2].

2. It was shown that electropositive substituents in arylmercury chlorides of type p-XC_6H_4-HgCl accelerate, and electronegative substituents retard the studied isotopic exchange reaction.

3. It was found that all of the investigated arylmercury chlorides react more rapidly with metallic mercury than do the corresponding diarylmercury compouds.

4. The mechanism of the reaction was discussed.

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* Original Russian pagination. See C. B. Translation.

STEREOCHEMISTRY OF THE SYMMETRIZATION OF 2-CHLORO-MERCURICAMPHANE UNDER THE INFLUENCE OF HYDRAZINE HYDRATE AND SODIUM STANNITE

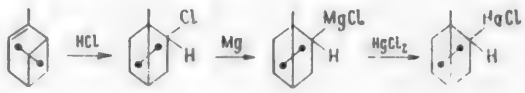
O. A. Reutov and Tsin-Chzhu Lu

In studying the symmetrization of 3-bromomercuricamphors under the influence of hydrazine hydrate [1] it was established that racemization occurs in all cases.* However, it was impossible to establish here whether this effect is due to the stereochemistry of the symmetrization reaction itself or whether the reaction goes with retention of configuration, and then the symmetrical organomercury compound formed suffers secondary racemization under the influence of hydrazine hydrate.

For a number of reasons, attempts to elucidate the stereochemistry of the symmetrization reaction under the influence of hydrazine hydrate on the example of 3-alkyl-3-bromomercuricamphor derivatives also proved unsuccessful [1].

In view of this we decided to transfer to those organomercury compounds of camphane that are not α-mercurated derivatives of carbonyl compounds.

First, we examined the possibility of obtaining organomercury derivatives of camphane from α-pinene by the scheme.



The α-pinene** used by us consisted of 50% d-α-pinene and 50% d, l-α-pinene. It had $[\alpha]^{18}D$ + 26.9°. Literature [2]: d-α-pinene $[\alpha]^{18}D$ + 53.9°; l-α-pinene $[\alpha]^{18}D$ - 54.04°.

The 2-chloromercuricamphane obtained from this pinene is a colorless crystalline substance (needles), readily soluble in acetone, dioxane, benzene and chloroform, and more difficultly soluble in ether, ethyl alcohol and methyl alcohol. 2-Chloromercuricamphane*** is extremely stable; it is not decomposed by mineral

* Here and later the terms "racemization" and "retention of configuration" refer to the assymmetric carbon atom attached to mercury.

** α-Pinene with $[\alpha]^{18}D$ + 26.9° was obtained by the rectification of turpentine, isolated from pine resin.

*** Bromomercuricamphane was obtained from 2-chloromercuricamphane.

$$C_{10}H_{17}—HgCl \xrightarrow{KOH} C_{10}H_{17}—HgOH \xrightarrow{HBr} C_{10}H_{17}—HgBr$$

2-Bromomercuricamphane was also obtained by reacting mercuri-bis-camphene with mercuric bromide and from bornyl chloride through the Grignard compound.

$$(C_{10}H_{17})_2Hg + HgBr_2 \longrightarrow 2C_{10}H_{17}—HgBr$$

$$C_{10}H_{17}Cl \xrightarrow{Mg} C_{10}H_{17}MgCl \xrightarrow{HgBr_2} C_{10}H_{17}—HgBr$$

acids even when heated, but is decomposed slowly by a mixture of fuming nitric and concentrated sulfuric acids, and also by aqua regia.

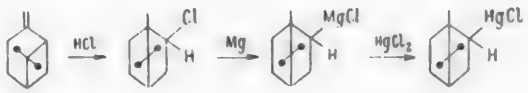
The obtained 2-chloromercuricamphane is a complex mixture of stereoisomers; we were able to isolate only one pure diastereomer from this mixture.

Since stereochemically pure α-pinene (not containing the racemic form as impurity) is found with great rarity in pine resin, to synthesize the diastereomeric 2-chloromercuricamphanes, differing in configuration only at carbon atom 2, we decided to use pure l-β-pinene.

We obtained l-β-pinene with $[\alpha]^{18}D$ −20.1° by the fractional distillation of turpentine from spruce resin through a column with an efficiency of 35 theoretical plates [3]: $[\alpha]^{18}D$ − 22.2°.

The bornylchloride that we obtained by reacting l - β-piene with hydrogen chloride had $[\alpha]^{18}D$ −33°. [2]: $[\alpha]^{18}D$ − 33.24°.

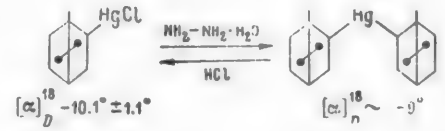
From bornyl chloride we obtained a mixture of the two diastereomers of 2-chloromercuricamphane (with $[\alpha]^{18}D$ ~0° and m. p. 155-157°), differing in configuration only at carbon atom 2, by the following scheme.



The mixture was recrystallized from ethyl alcohol (methyl alcohol, acetone or dioxane can be used also). Diastereomer (I) had m. p. 165-166° and $[\alpha]^{18}D$ − 10.1° ± 1°. Diastereomer II hadm. p. 169-170° and $[\alpha]^{18}D$ + 15.4° ± 1.2°. Both of the 2-chloromercuricamphane diastereomers are stable. The specific rotation does not change when tney are boiled in either ethyl alcohol or xylene solution. •

2-Chloromercuricamphane is not symmetrized with either ammonia or sodium thiosulfate, but is easily symmetrized with hydrazine hydrate and sodium stannite.

The symmetrization of diastereomer (I) with $[\alpha]^{18}D$ − 10.1° ± 1.0° using hydrazine hydrate was effected by boiling its alcohol solution for 1 hour with a 2-fold excess of hydrazine hydrate. The mercuri-bis-camphane obtained in this manner had m. p. 145-150° (decomp.) and $[\alpha]^{18}D$ − 9°; the substance is extremely unstable and decomposes even in the cold with the separation of metallic mercury. The mercuri-bis-camphane obtained in this manner proved to be a pure diastereomer. This derives from the fact that when recrystallized mercuri-bis-camphane was reacted with hydrogen chloride in ethyl alcohol we obtained the pure diastereomer (I) 2-chloromercuricamphane with $[\alpha]^{18}D$ -10.6° ± 1.1°.



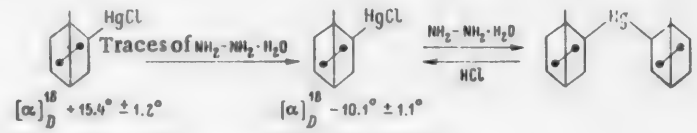
As a result, the symmetrization of diastereomer (I) with hydrazine hydrate proceeds with retention of the configuration for the carbon atoms found in position 2 of both of the 2-chloromercuricamphane molecules reacting.

The symmetrization of diastereomer (II) with $[\alpha]^{18}D$ 15.4° ± 1.2°, and m. p. 169-170°, using hydrazine hydrate, was accomplished in a similar manner. When the recrystallized symmetrical product obtained from this reaction was reacted with hydrogen chloride in ethyl alcohol we obtained pure diastereomer (I) with $[\alpha]^{18}D$ − 10.9° ± 2.2° and m. p. 165-166°.

• The specific rotation of the mixture of 2-chloromercuricamphane diastereomers, obtained from α-pinene, changes when the mixture is boiled in xylene. This is apparently due to the instability of some of the diastereomers present in the mixture.

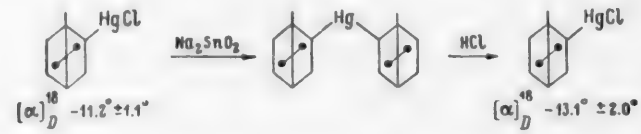
That the same symmetrical organomercury compound is formed irrespective of whether diastereomer (II) or diastereomer (I) is symmetrized with hydrazine hydrate is explained by the fact that at the start the less stable diastereomer (II) under the influence of hydrazine hydrate is converted to the more stable diastereomer (I), which then undergoes symmetrization.

The validity of such a mechanism for the symmetrization of diastereomer (II) was confirmed by special experiments, in which it was shown that diastereomer (II) is easily converted to diastereomer (I) in the presence of even trace amounts of hydrazine hydrate:

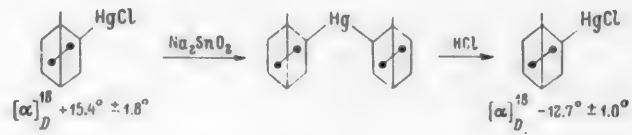


(Diastereomer II) (Diastereomer I)

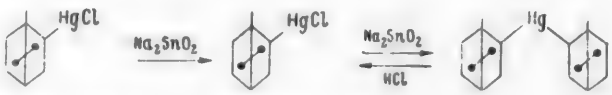
Symmetrization of the 2-chloromercuricamphane diastereomer (I) with $[\alpha]^{18}D - 11.2° \pm 1.1°$, using sodium stannite, was run with an equimolar amount of sodium stannite in the cold for 2 hours with vigorous stirring. The crude mercuri-bis-camphane obtained from this reaction when reacted with hydrogen chloride gave the 2-chloromercuricamphane diastereomer (I) with $[\alpha]^{18}D - 13.1° \pm 2°$.



The symmetrization of diastereomer (II) with $[\alpha]^{18}D + 15.1° \pm 1.8°$, using sodium stannite, was done in the same manner. It proved that when the crude mercuri-bis-camphane obtained here was reacted with hydrogen chloride in ethyl alcohol we obtained diastereomer (I) with $[\alpha]^{18}D - 12.7° \pm 1°$.



From these results it follows that the symmetrization of diastereomer (I) with sodium stannite proceeds with retention of the configuration for the carbon atoms found in position 2 of both of the 2-chloromercuricamphane molecules reacting. As regards the symmetrization of diastereomer (II) with sodium stannite, then apparently here diastereomer (II), under the influence of sodium stannite, is first isomerized to the more stable diastereomer (I), which then undergoes symmetrization. The situation here is completely analogous to that existing for the symmetrization of diastereomer (II) with hydrazine hydrate.

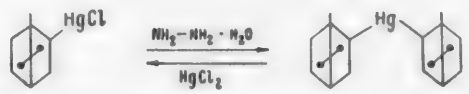


(Diastereomer II) +(Diastereomer II)

The above results could also be explained by assuming that the symmetrization of diastereomer (I) with either hydrazine hydrate or sodium stannite actually proceeds with configuration inversion of the involved carbon atom. As a result, a mercuri-bis-camphane should be formed here in which the carbon atoms in positions 2 and 2' have opposite configurations. Since the stability of the bonds between mercury and the carbon atoms (2 and 2') in the mercuri-bis-camphane could be quite different in such a case, then when this mercuri-bis-cam-

phane is reacted with hydrogen chloride the weaker bond should suffer cleavage with the formation of the more stable 2-chloromercuricamphane diastereomer (I). However, such a theory becomes highly improbable in view of the fact that when mercuri-bis-camphane (obtained by the symmetrization of pure diastereomer (I) using hydrazine hydrate) is reacted with mercuric chloride only one diastereomer (I) is formed.

As a matter of fact, reaction of the symmetrical product, obtained by the symmetrization using hydrazine hydrate of the 2-chloromercuricamphane diastereomer (I) with $[\alpha]^{18}D$ – 10.1° ± 1.1°, with mercuric chloride in acetone under reflux for 3 hours yields pure diastereomer (I) with $[\alpha]^{18}D$ – 9.2°± 1°.



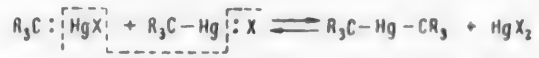
(Diastereomer I)

Secondary isomerization due to one of the diastereomeric 2-chloromercuricamphanes reacting with the mercuric chloride cannot be superimposed on this result, for even the less stable diastereomer (II) does not change its angle of rotation when reacted with mercuric chloride in refluxing acetone for 3 hours.

As is known [4-6], reaction of symmetrical organomercury compounds with mercury halides, representing electrophilic substitution on a tetrahedral carbon atom, proceeds with retention of the stereochemical configuration. In view of this, the stereochemical result obtained in the reaction of mercuri-bis-camphane with mercuric chloride is evidence that, in the mercuri-bis-camphane obtained by the symmetrization of diastereomer (I) using hydrazine hydrate the configuration at atoms 2 and 2' is the same; consequently, the symmetrization of diastereomer (I) under the influence of hydrazine hydrate (or sodium stannite) proceeds with retention of the configuration.

In conclusion we will examine one of the aspects of the mechanism for the reactions studied by us.

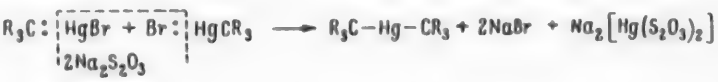
The fact that, independent of the symmetrization agent used, symmetrization in our cases proceeds with retention of the stereochemical configuration [7, 5] could be explained by assuming that in all of the cases studied by us an equilibrium exists between organomercury salt, symmetrical organomercury compound and mercury halide.*



The symmetrization agent reacts with mercury halide, causing the equilibrium to shift to the right.

The same stereochemical result in this case is explained by the fact that in all cases the symmetrical compound is formed as the result of bimolecular electrophilic substitution on a saturated carbon atom (S_E2).

However, without special kinetic studies, it is impossible to exclude the possibility that the symmetrization reactions studied by us progress as the result of direct reaction between organomercury salt and symmetrization agent. In such case the symmetrization of 3-bromomercuricamphors with sodium thiosulfate, proceeding with retention of configuration [10], represents the following electrophilic substitution reaction:



* It has been definitely shown in a number of cases [8, 9] that the symmetrization reaction goes through the indicated equilibrium stage.

It is possible for symmetrization with hydrazine hydrate * to represent homolytic substitution on the carbon atom.

$$2\,R_3C\cdot + HgBr_2 + 2Br\cdot + Hg(CR_3)_2 \xrightarrow{5NH_2-NH_2\cdot H_2O} R_3C-Hg-CR_3 + N_2 + 2Hg + 5H_2O + 4NH_2-NH_2\cdot HBr$$

The retention of configuration, unusual for radical substitution, was probably due to the fact that the subjects used in our investigation were not optical antipodes, but instead were diastereomers, possessing different stability. For the case of the more stable diastereomer, the configuration of the carbon atom involved can apparently be retained even during radical substitution.

EXPERIMENTAL

1. Preparation of bornyl chloride from α-pinene. From 400 g of α-pinene with b. p. 155-156° and $[\alpha]^{18}D$ + 26.7° we obtained 292 g (52%) of bornyl chloride.

M.p. 132°, $[\alpha]^{18}D$ + 18.1° (in ethyl alcohol). Literature data for d-bornyl chloride [2]: m.p. 132°, $[\alpha]^{18}D$ + 33.5°.

2. Preparation of 2-chloromercuricamphane from d-bornyl chloride. Ten grams of magnesium turnings in a 3-necked flask were covered with a solution of 50 g of d-bornyl chloride, with $[\alpha]^{18}D$ + 18.1°, in 200 ml of absolute ether. After stirring for 4 hours with heating (all of the magnesium dissolved) the solution was filtered rapidly through glass wool, after which it was transferred to a 3-necked flask, fitted with stirrer, reflux condenser and nitrogen inlet tube. The solution was treated in 1 hour with 78 g of mercuric chloride in a steady nitrogen stream. The reaction mixture was refluxed for 4 hours and then allowed to stand overnight. The ether was distilled off, while the residue was treated with a mixture of ice and dilute hydrochloric acid solution. The obtained precipitate was washed with a small amount of alcohol, then with 500 ml of hot water, and again with a small amount of alcohol. The crude product was recrystallized from either alcohol, glacial acetic acid or acetone. 2-Chloromercuricamphane was obtained as white needles, readily soluble in ether, acetone, benzene, toluene, xylene and dioxane, more difficultly soluble in methyl and ethyl alcohols and in glacial acetic acid, and insoluble in water. The substance remains stable when heated with either concentrated hydrochloric or sulfuric acid, but is decomposed slowly with either aqua regia or a mixture of concentrated sulfuric and fuming nitric acids. The yield of 2-chloromercuricamphane was 20 g (20%). M. p. 169-170°.

Found %: C 32.06, 32.22; H 4.67; 4.66. $C_{10}H_{17}HgCl$. Calculated %: C 32.17; H 4.57.

The 2-chloromercuricamphane obtained in this manner is a complex mixture of diastereomers. Attempts to isolate even a single pure diastereomer by fractional crystallization of the mixture from various solvents (methyl, ethyl, isoamyl alcohols, acetone, ethyl acetate, acetic acid) proved unsuccessful. The specific rotation in the different experiments ranged from -7 to + 12°, while the m. p. varied from 153 to 171°.

3. Symmetrization of 2-chloromercuricamphane with sodium stannite. A solution of 11 g of 2-chloromercuricamphane in hot acetone was treated with 140 ml of water, and the suspension thus obtained was treated with alkaline sodium stannite solution (prepared from 9.2 g of sodium hydroxide, 7.3 g of $SnCl_2 \cdot 2H_2O$ and 200 ml of water). The reaction mixture was stirred for 3 hours. The precipitate was filtered and then extracted with boiling acetone. The acetone was evaporated, while the solid residue was recrystallized from alcohol. Yield of 2,2'-mercuri-bis-camphane 2 g (30%). The compound was obtained as colorless needles, decomposing quite readily when stored (quite dark after 12 hours). M. p. 130-135° (decomp.).

Found %: Hg 42.01, 42.13. $(C_{10}H_{17})_2Hg$. Calculated %: Hg 42.22.

4. Reaction of 2,2'-mercuri-bis-camphane with hydrogen chloride. A stream of dry hydrogen chloride was passed into a solution of 2-g of 2,2'-mercuri-bis-camphane in 200 ml of alcohol for 3 hours. The solution

* The mechanism for symmetrization with sodium stannite is apparently analogous to the mechanism for symmetrization with hydrazine hydrate.

was evaporated to half volume, and the obtained precipitate of 2-chloromercuricamphane was filtered and then recrystallized from alcohol. M. p. 170-171°.

Found %: C 32.58; 32.51; H 4.74, 4.64. $C_{10}H_{17}HgCl$. Calculated %: C 32.17; H 4.57.

5. Preparation of 2-bromomercuricamphane from 2-chloromercuricamphane. A solution of 0.9 g of 2-chloromercuricamphane, with $[\alpha]^{18}D$ + 11° ± 0.5° and m. p. 169-171°, in 5 ml of alcohol was treated with 2 ml of alcoholic potassium hydroxide solution containing 0.2 g of KOH, after which the reaction mixture was heated for 30 minutes on the water bath with shaking. The precipitate of potassium chloride was filtered, and the filtrate was treated with concentrated hydrobromic acid until neutral. The obrained precipitate of 2-bromomercuricamphane was filtered, and then washed with water with alcohol. Yield 0.67 g (67%).

M.p. 183-185°, m.p. 186-188° (from methyl alcohol], $[\alpha]^{18}D$ + 14.1° ± 0.7°.

Found %: C 28.98, 28.27; H 4.26, 4.27. $C_{10}H_{17}HgBr$. Calculated %: C 28.78; H 4.11.

6. Preparation of l-β-pinene from turpentine obtained from spruce resin. A mixture of 200 g of spruce resin and 35 g of sodium hydroxide was heated in a 500-ml round-bottomed flask until a homogeneous dark-brown mass was obtained; after this the mixture was steam-distilled. The distillate was allowed to stand for a day, after which the oil (about 40 g) was separated and dried over potassium carbonate. The fraction with b. p. 163-165° was collected when the material was distilled through a column (35 theoretical plates). Yield of l-β-pinene 10 g.

$[\alpha]^{18}D$ −20.1°, $n^{20}D$ 1.4780. Literature [3]: $[\alpha]_D$ − 22.1, b. p. 164°, $n^{20.5}D$ 1.4773.

7. Preparation of l-bornyl chloride from l-β-pinene. Into a 250-ml 3-necked flask, fitted with stirrer, thermometer and both a gas-inlet and a gas-outlet tube, was charged 200 g of l-β-pinene (obtained in Expt. 6), and then a stream of dry hydrogen chloride was passed through the liquid until (about 6 hours) it began to thicken. The temperature of the reaction mixture was maintained constant at 15-20° by external cooling. At reaction end, the mixture was cooled to −10 to −15°, and then kept at this temperature for 2 hours. The obtained crystals were filtered, while the mother liquor was cooled to low temperature a second time. Yield of l-bornyl chloride 120 g (50%).

M.p. 110-115°; b. p. 132 (from alcohol, $[\alpha]^{18}D$ − 33°. Literature [2]: m.p. 132°, $[\alpha]_D$ − 33.24°.

8. Preparation of 2-chloromercuricamphane from l-bornyl chloride. 2-Chloromercuricamphane was obtained (using the method of Expt. 2) from 10 g of magnesium, 50 g of l-bornyl chloride and 78 g of mercuric chloride in 200 ml of absolute ether. Yield of 2-chloromercuricamphane 20 g (20%). M.p. 158-160° $[\alpha]^{18}D$ ~ 0°.

9. Separation of mixture of 2-chloromercuricamphane diastereomers. The mixture (25 g) of 2-chloromercuricamphane diastereomers, with $[\alpha]^{18}D$ ~0°, was dissolved in 300 ml of boiling ethyl alcohol, and the solution was filtered hot. The filtrate on cooling gave 12.5 g of precipitate with $[\alpha]^{18}D$ + 3.8° ± 0.6° (c 4.84,* l 1.9, α + 0.35 ± 0.05°). After a second recrystallization from 100 ml of ethyl alcohol we obtained 5.5 g of precipitate with $[\alpha]^{18}D$ + 9.0° ± 0.6° (c 4.60, l 1.9, α + 0.8° ± 0.05°). After a third recrystallization from 50 ml of acetone we obtained 2 g of substance with $[\alpha]^{18}D$ + 12.1° ± 0.6° (c 4.34, l 1.9, α + 1.0° ± ± 0.05°). After a fourth recrystallization from 25 ml of acetone we obtained pure diastereomer (II) with m. p. 169-170° and $[\alpha]^{18}D$ + 15.4° ± 1.2° (c 2.17, l 1.9, α + 0.65° ± 0.05°). Further recrystallization of the substance from acetone failed to change the angle of rotation.

Found %: C 32.32, 32.24; H 4.59, 4.67. $C_{10}H_{17}HgCl$. Calculated %: C 32.17; H 4.57.

We used the filtrate from the first recrystallization of 25 g of mixed diastereomers from 300 ml of ethyl alcohol to isolate diastereomer (I). This filtrate was evaporated to dryness. The solid residue had $[\alpha]^{18}D$ −3.4° ± 0.3° (c 4.66, l 1.9, α − 3.0° ± 0.05°). Recrystallization of this residue from 250 ml of ethyl alcohol gave 4.0 g of substance with $[\alpha]^{18}D$ ~0°. The filtrate from the separation of this material was evaporated to

* In all cases the concentration c is expressed in grams of substance per 100 ml of solvent (anhydrous acetone).

half volume. Here we obtained 2.1 g of precipitate with $[\alpha]^{18}D$ – 6.8° ± 0.5° (c 4.67, l 1.9, α – 0.6° ± 0.05°). The filtrate from the separation of this precipitate was again evaporated to half volume. Here we obtained 1.2 g of precipitate with $[\alpha]^{18}D$ – 7.9 ± 0.7° (c 3.66, l 1.9, α – 0.55° ± 0.05°). The filtrate after the removal of this precipitate was evaporated to dryness. The solid residue had $[\alpha]^{18}D$ – 9.6° ± 1.0° (c 2.78, l 1.9, α – 0.50° ± 0.05°). This residue was recrystallized from acetone. The obtained precipitate was filtered and the filtrate was evaporated to half volume. Here we obtained the pure diastereomer (I) with m. p. 165-166° and $[\alpha]^{18}D$ – 10.1 ± 1.0° (c 2.6, l 1.9, α – 0.50° ± 0.5°). Further recrystallization failed to change the specific rotation of the substance.

Found %: C 32.15, 32.20; H 4.66, 4.63. $C_{10}H_{17}HgCl$. Calculated %: C 32.17; H 4.57.

The two diastereomers can also be separated by fractional recrystallization from 85% aqueous dioxane.

10. Symmetrization of 2-chloromercuricamphane diastereomer (I) with hydrazine hydrate. Three grams of diastereomer (I) with $[\alpha]^{18}D$ – 10.1° ± 1.0° were dissolved in 25 ml of hot ethyl alcohol. Then 2.5 g of hydrazine hydrate and 1.2 g of potassium carbonate were added to the solution. The mixture was heated under reflux for 1 hour, then filtered, and the filtrate evaporated to dryness. The solid residue was washed with water and then with a small amount of alcohol. Yield of 2,2'-mercuri-bis-camphane 0.9 g (50%). After recrystallization from ethyl alcohol, m. p. 145-150° (decomp.) and $[\alpha]^{18}D$ – 9.2° ± 1.0° (c 2.85, l 1.9, α – 0.5° ± 0.05°).

Found %: Hg 42.33, 42.47. $(C_{10}H_{17})_2Hg$. Calculated %: Hg 42.22.

11. Reaction of 2,2'-mercuri-bis-camphane (obtained by the symmetrization of diastereomer (I) with hydrazine hydrate) with hydrogen chloride. A solution of 0.7 g of recrystallized 2,2'-mercuri-bis-camphane, obtained in Expt. 10, in 20 ml of ethyl alcohol was treated with a stream of dry hydrogen chloride for 2 hours. The solution was evaporated to half volume, and the obtained crystals of 2-chloromercuricamphane were filtered, washed with water, and then with a little acetone. Yield 0.4 g (73%).

M.p. 162-163°, $[\alpha]^{18}D$ – 10.6° ± 1.1° (c 2.71, l 1.9, α – 0.55° ± 0.05°).

Found %: C 32.14, 32.33; H 4.63, 4.69. $C_{10}H_{17}HgCl$. Calculated %: C 32.17; H 4.57.

12. Symmetrization of 2-chloromercuricamphane diastereomer (II) with hydrazine hydrate. A solution of 1.1 g of diastereomer (II) with $[\alpha]^{18}D$ + 15.4° ± 1.2° was prepared by dissolving in 25 ml of hot ethyl alcohol. Then 0.4 g of hydrazine hydrate and 0.3 g of potassium carbonate were added to this solution, after which the reaction mixture was refluxed for 3 hours. The precipitate was filtered from the solution, and the filtrate was evaporated to dryness. The residue was washed with water and then with a little ethyl alcohol. Yield of 2,2'-mercuri-bis-camphane 0.35 g (63%). After recrystallization from ethyl alcohol, m. p. 143-150° (decomp.) and $[\alpha]^{18}D$ –7.3 ± 1.2° (c 2.18, l 1.9, α – 0.3° ± 0.05).

13. Reaction of mercuri-bis-camphane (obtained by the symmetrization of 2-chloromercuricamphane diastereomer (II) with hydrazine hydrate) with hydrogen chloride. A stream of dry hydrogen chloride was passed for 2 hours into a solution of 0.35 g of crude 2,2'-mercuri-bis-camphane, obtained in Expt. 12, in 20 ml of ethyl alcohol. The solution was then evaporated to half volume, and the obtained crystals of 2-chloromercuricamphane diastereomer (I) filtered, washed with water, and then with a little acetone. Yield 0.17 g (62%).

M.p. 163-165°, $[\alpha]^{18}D$ – 10.9° ± 2.2° (c 2.28; l 1.9, α – 0.25° ± 0.05°).

Found %: C 32.11, 32.24; H 4.60, 4.64. $C_{10}H_{17}HgCl$. Calculated %: C 32.17; H 4.57.

14. Symmetrization of 2-chloromercuricamphane diastereomer (I) with sodium stannite. A solution of 2 g of diastereomer (I), with $[\alpha]^{18}D$ – 11.2° ± 1.1°, in hot acetone was poured into 30 ml of water and the thus obtained suspension was treated with alkaline sodium stannite solution (obtained from 1.66 g of NaOH, 1.32 g of $SnCl_2 \cdot 2H_2O$ and 40 ml of water). The reaction mixture was stirred for 3 hours. The precipitate was filtered and extracted with boiling acetone. The solvent was evaporated from the acetone extract. Yield of 2,2'-mercuri-bis-camphane 0.5 g (40%). After recrystallization from ethyl alcohol, m. p. 145-150°.

15. Reaction of mercuri-bis-camphane (obtained by the symmetrization of 2-chloromercuricamphane diastereomer (I) with sodium stannite) with hydrogen chloride. Dry hydrogen chloride was passed for 2 hours into a solution of 0.5 g of crude 2,2'-mercuri-bis-camphane, obtained in Expt. 14, in 20 ml of alcohol. The

solution was evaporated to half volume. The obtained needles of 2-chloromercuricamphane diastereomer (I) were filtered, washed with water, and then with a little acetone. Yield 0.2 g (50%).

M.p. 164-166°, $[\alpha]^{18}D$ − 1.3.1° ± 2° (c 1.41, l 1.9, α− 0.35° ± 0.05°).

16. Symmetrization of 2-chloromercuricamphane diastereomer (II) with sodium stannite. Two grams of diastereomer (II) with [ ]^{18}D + 15.4 1.2° was dissolved in hot acetone, and the solution then poured into 30 ml of water. The obtained suspension was treated with alkaline sodium stannite solution (obtained from 1.66 g of NaOH, 1.32 g of $SnCl_2 \cdot 2H_2O$ and 40 ml of water). The reaction mixture was stirred in the cold for 3 hours, after which the precipitate was filtered and then extracted with boiling acetone. The solvent was evaporated from the acetone extract. Yield of 2,2'-mercuri-bis-camphane 0.65 g (51%). After recrystallization from ethyl alcohol, m. p. 143-149° (decomp.).

17. Reaction of mercuri-bis-camphane (obtained by the symmetrization of 2-chloromercuricamphane diastereomer (II) with sodium stannite with hydrogen chloride. A stream of dry hydrogen chloride was passed for 2 hours into a solution of 0.65 g of crude mercuri-bis-camphane, obtained in Expt. 16, in 20 ml of ethyl alcohol, after which the solution was evaporated to half volume. The obtained crystals of 2-chloromercuricamphane diastereomer (I) were filtered, washed with water, and then with a little acetone. Yield 0.35 g (70%).

M.p. 166-167°, $[\alpha]^{18}D$ − 12.7° ± 1.0° (c 2.48, l 1.9, α− 0.6° ± 0.05°).

18. Heating of 2-chloromercuricamphane diastereomer (II) in ethyl alcohol in the presence of hydrazine hydrate. A solution of 0.3 g of diastereomer (II), with $[\alpha]^{18}D$ + 15.4° ± 1.2°, in 25 ml of ethyl alcohol was treated with 6 drops of hydrazine hydrate. The solution was refluxed for 3 hours, filtered, and then evaporated to dryness. Weight of solid residue 0.26 g.

M.p. 166-167° $[\alpha]^{18}D$ - 7.2° ± 1.4° (c 1.85, l 1.9, α − 0.25° ± 0.05°).

Found %: C 32.25, 32.09; H 4.41, 4.65. $C_{10}H_{17}HgCl$. Calculated %: C 32.17; H 4.57.

19. Reaction of 2,2'-mercuri-bis-camphene (obtained by the symmetrization of 2-chloromercuricamphane diastereomer (I) with hydrazine hydrate) with mercuric chloride. A mixture of 0.5 g of crude mercuri-bis-camphane, obtained in Expt. 10, and 0.27 g of mercuric chloride was dissolved in 30 ml of acetone. The obtained solution was refluxed for 3 hours. The acetone was evaporated, and the dry residue was washed with hot water until mercuric chloride was absent in the wash water. Yield of 2-chloromercuricamphane diastereomer (I) 0.6 g (77%).

M.p. 165-166°, $[\alpha]^{18}D$ − 9.2° ± 1.0° (c 2.58, l 1.9, α− 4.5° ± 0.05°).

Found %: C 32.34, 34.14; H 4.75, 4.61. $C_{10}H_{17}HgCl$. Calculated %: C 32.17; H 4.57.

SUMMARY

1. The diastereomers of 2-chloromercuricamphane, differeing in stereochemical configuration only at carbon atom 2, were synthesized and isolated pure.

2. It was shown that the symmetrization of the more stable 2-chloromercuricamphane diastereomer (I) with $[\alpha]^{18}D$ − 10.1 ± 1.0°, using either hydrazine hydrate or sodium stannite, proceeds with retention of the stereochemical configuration for the carbon atom involved in the reaction.

3. It was shown that the less stable 2-chloromercuricamphane diastereomer (II), with $[\alpha]^{18}D$ + 15.4 ± 1.2°, is isomerized under the influence of hydrazine hydrate to the more stable diastereomer (I).

4. The mechanism of the symmetrization reaction was discussed.

5. It was shown that the reaction of mercuri-bis-camphane with mercuric chloride proceeds with retention of the stereochemical configuration for the carbon atom involved.

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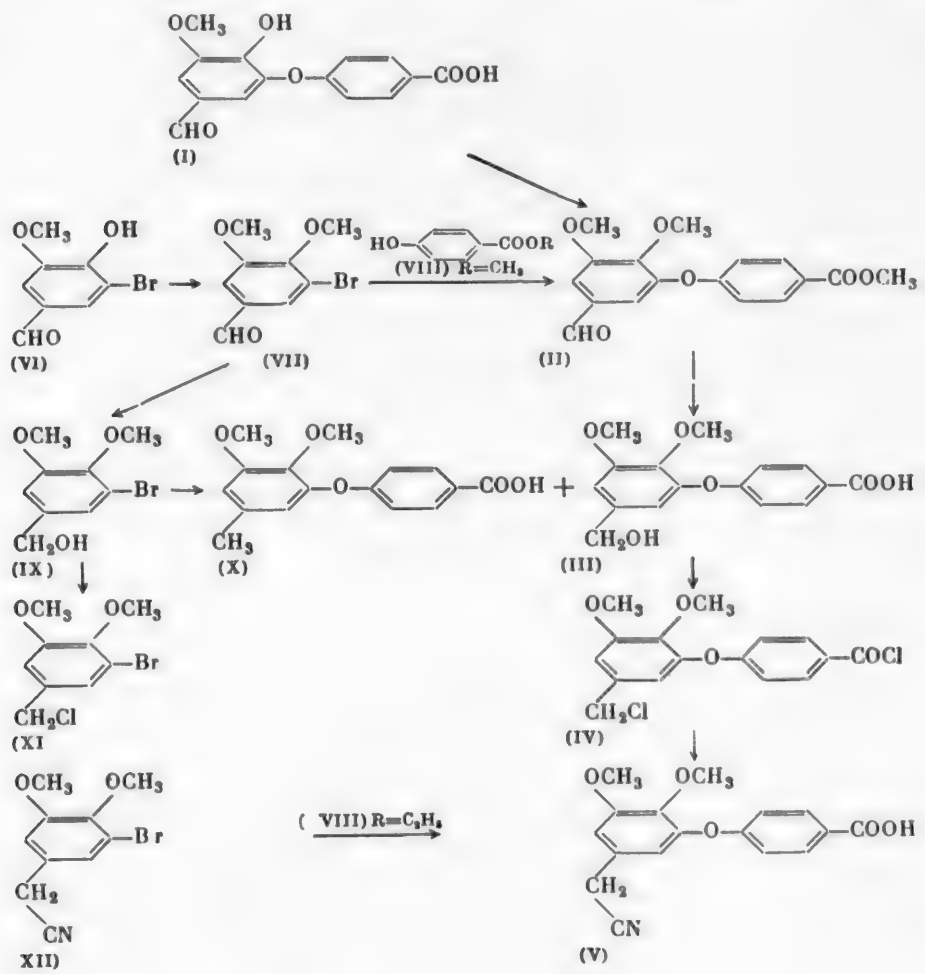
SYNTHESES OF CURARE ALKALOIDS

SYNTHESIS OF 2,3-DIMETHOXY-5-CYANOMETHYL-4'-CARBOXYDIPHENYL ETHER

O. N. Tolkachev, A. A. Cherkasova, and N. A. Preobrazhenskii

In the previous paper [1], we had published the synthesis of 2-hydroxy-3-methoxy-5-(β-nitrovinyl)-4'-carboxydiphenyl ether serving as an intermediate in the synthesis of the tube carare alkaloids: tubocurarine and isochondodendrine. The phenylethylamine portion of these alkaloids, β-[3-methoxy-4-alkoxy-5-(4'-carbalkoxyphenoxy)-phenyl]-ethylamine, may be synthesized by two alternate routes; 1) via 2-hydroxy-3-methoxy-5-(β-nitrovinyl)-4'-carboxydiphenyl ether, described in the previous paper, and 2) via nitrile (V).



In this paper, we describe the synthesis of 2,3-dimethoxy-5-cyanomethyl-4'-carboxydiphenyl ether (V). Conversion of the functional groups, for example, methylation of the hydroxyl, reduction of the aldehyde group to the alcohol, and transition from the alcohol to the nitrile group, can be effected at various stages in the synthesis, as can be seen from the above scheme.

2-Hydroxy-3-methoxy-5-formyl-4'-carboxydiphenyl ether (I) was methylated with either methyl iodide or dimethyl sulfate in alkaline medium to 2,3-dimethoxy-5-formyl-4'-carbomethoxydiphenyl ether (II), identical with the product obtained by the condensation of 5-bromoveratraldehyde (VII) with methyl 4-hydroxybenzoate (VIII, R = CH_3). Reduction (Cannizzaro) of ether (II) leads to 2,3-dimethoxy-5-hydroxymethyl-4'-carboxydiphenyl ether (III). The same substance, together with 2,3-dimethoxy-5-methyl-4'-carboxydiphenyl ether (X), is obtained by the condensation of 5-bromoveratryl alcohol (IX) with methyl 4-hydroxybenzoate (VIII, R = CH_3). Compound (III) when treated with thionyl chloride is converted to 2,3-dimethoxy-5-chloromethyl-4'-chlorocarbonyldiphenyl ether (IV), which is then cyanided to 2,3-dimethoxy-5-cyanomethyl-4'-carboxydiphenyl ether (V), identical with the compound obtained by the condensation of 3,4-dimethoxy-5-bromobenzyl cyanide (XII) with ethyl 4-hydroxybenzoate (VIII, R = C_2H_5).

The intermediates used in the synthesis were obtained in the following manner. Bromination of vanillin with dioxane dibromide gave 5-bromovanillin (VI), which was then methylated with dimethyl sulfate to 5-bromoveratryl alcohol (IX). Treatment of (IX) with thionylchloride gave 3,4-dimethoxy-5-bromobenzyl chloride (XI), which with NaCN was converted to 3,4-dimethoxy-5-bromobenzyl cyanide (XII).

EXPERIMENTAL

1. 2,3-Dimethoxy-5-formyl-4'-carbomethoxydiphenyl ether (II). a) To a solution of 1.15 g of potassium hydroxide and 3 g of methyl 4-hydroxybenzoate in 15 ml of anhydrous methyl alcohol were added 5 g of 5-bromoveratraldehyde and 3 g of copper powder. After removal of the alcohol and water in vacuo, the residue was heated in a nitrogen stream for 2 hours at 200-205°. The reaction mixture was cooled, ground, and digested with ether (4 times with 50 ml portions). The extract was filtered, washed with 10% aqueous sodium hydroxide (3 times with 20 ml portions), then with water (twice with 20 ml portions), dried over sodium sulfate, and concentrated in vacuo. The orange, oily substance obtained (2.99 g) crystallized on long standing. It was stirred with ethyl alcohol and the precipitate of 2,3-dimethoxy-5-formyl-4'-carbomethoxydiphenyl ether was separated. Yield 0.04 g (0.62%). M. p. 109-110° (from methyl alcohol).

Found %: C 64.93, 64.68; H 4.97, 5.28. $C_{17}H_{16}O_6$. Calculated %: C 64.6; H 5.07.

b) To a solution of 0.21 g of 2-hydroxy-3-methoxy-5-formyl-4'-carboxydiphenyl ether in 30 ml of methyl alcohol and 0.2 g of KOH in 0.42 ml of water was added 2.3 g of methyl iodide, and the mixture heated under reflux for 2.5 hours. The alcohol and excess methyl iodide were removed in vacuo, while the residue was treated with 10 ml of 3% aqueous NaOH solution and then extracted with ether (3 times with 20 ml portions). Acidification of the water layer with hydrochloric acid gave 0.04 g of unreacted starting material. The ether extract after drying over sodium sulfate was evaporated. Yield of 2,3-dimethoxy-5-formyl-4'-carbomethoxydiphenyl ether 0.08 g (42.9%, based on reacted diphenyl ether I). M. p. 109.5-110° (from methyl alcohol).

Found %: C 64.4, 64.82; H 4.77, 4.70. $C_{17}H_{16}O_6$. Calculated %: C 64.55; H 5.09.

The mixed melting point with the substance obtained in the preceding experiment was not depressed.

2. 2,3-Dimethoxy-5-hydroxymethyl-4'-carboxydiphenyl ether (III). a) To a solution of 1.75 g of 2,3-dimethoxy-5-formyl-4'-carbomethoxydiphenyl ether (II) in 50 ml of methyl alcohol and 2 ml of 28% aqueous formaldehyde was added in drops a solution of KOH in 1.2 ml of alcohol in 5 minutes at 30°, after which the mixture was heated for 25 minutes at 60° and then for 1.5 hours at boiling. The alcohol was vacuum-distilled, while the residue was treated with 40 ml of water, filtered, and the filtrate acidified with dilute (1:1) hydrochloric acid. The obtained precipitate (1.29 g) was separated, treated with hot saturated sodium bisulfite solution (3 times with 10 ml portions), then with hot benzene (5 times with 10 ml portions), followed by removal of the benzene in vacuo to leave a colorless crystalline substance. M. p. 173-174° (from alcohol).

Found %: C 63.20, 63.17; H 5.53, 5.01. $C_{16}H_{16}O_6$. Calculated %: C 63.20, H 5.27.

b) To a solution of 0.72 g of KOH, 3.75 g of ethyl 4-hydroxybenzoate (VIII, R = C_2H_5) and 3 g of 5-bromoveratryl alcohol (IX) in 15 ml of methyl alcohol was added 3 g of copper catalyst. The alcohol was vacuum-distilled, while the residue was heated at 180-186° for 1 hour. The reaction mass after cooling was rubbed with ether, and the extract was first washed with 3% NaOH solution and then concentrated in vacuo. The residue (1.49 g) was heated at 95-100° with a solution of 5 g of NaOH in 10 ml of water for 1.5 hours. The reaction mass was diluted with 40 ml of water and the unsaponified portion extracted with ether (twice with 15 ml portions). The water layer was neutralized with dilute (1 : 1) hydrochloric acid, the resulting oily substance extracted with ether, the ether removed from the extract in vacuo, and the residue treated with alcohol to give 2,3-dimethoxy-5-methyl-4'-carboxydiphenyl ether (X). Colorless crystalline substance with m. p. 183-184° (from alcohol). Yield 0.03 g (0.86%).

Found %: C 66.70, 66.89; H 5.25, 5.99. $C_{16}H_{16}O_5$. Calculated %: C 66.70; H 5.56.

The alcohol mother liquors were evaporated, the residue diluted with a little ether, and the obtained precipitate of 2,3-dimethoxy-5-hydroxymethyl-4'-carboxydiphenyl ether (III) was filtered. Colorless crystalline substance with m. p. 174-176° (from alcohol). Yield 0.22 g (5.97%).

Found%: C 63.31, 63.46; H 5.29, 5.35. $C_{16}H_{16}O_6$. Calculated %: C 63.20; H 5.27.

The mixed melting point with the substance from the preceding experiment was not depressed.

3. 2,3-Dimethoxy-5-cyanomethyl-4'-carboxydiphenyl ether (V). a) A mixture of 0.10 g of 3,4-dimethoxy-5-chloromethyl-4'-chlorocarbonyldiphenyl ether (IV), obtained from 3,4-dimethoxy-5-hydroxymethyl-4'-carboxydiphenyl ether (III) by reacting with thionyl chloride, 13 ml of acetone, 1 g of sodium cyanide and 4 ml of water was heated under reflux for 7 hours. Then the solvent was distilled off, and the residue was dissolved in 8 ml of water, filtered, and acidified with dilute (1 : 1) hydrochloric acid. The obtained precipitate was filtered, then dissolved in methyl alcohol, the solution filtered, and after removal of the solvent the compound was precipitated from acetic acid. M. P. 154-156°. Yield 0.05 g (54.5%).

b) To a solution of 0.915 g of KOH in 20 ml of alcohol were added 7.8 g of ethyl 4-hydroxybenzoate (VIII, R = C_2H_5), 6 g of 3,4-dimethoxy-5-bromobenzyl cyanide (XII) and 6 g of copper catalyst. The alcohol was vacuum distilled, while the residue was heated for 1 hour at 190-200° in a nitrogen stream with mechanical stirring. The reaction mass after cooling was dissolved in 250 ml of ether and filtered from the copper; the ether extract was washed first with 5% NaOH solution, then with water, and after removal of the solvent, we obtained 2.51 g of oily substance. The insoluble residue was treated with 250 ml of chloroform, from which we obtained 6.03 g of substance. The latter was heated for 2 hours under reflux with 3 g of potassium carbonate, 30 ml of methyl alcohol, and 10 ml of water. The alcohol was distilled off, while the residue was dissolved in 100 ml of water, filtered, neutralized with dilute (1 : 1) hydrochloric acid, and the obtained precipitate (0.30 g) separated and then treated with 25 ml of boiling carbon tetrachloride. The residue was dissolved in dilute (1: 1) acetic acid (50 ml) with heating to 100°. The substance (weight 20 mg, m.p. 179 – 182°) obtained on cooling was separated, while the filtrate was diluted with 2 volumes of water, which gave the diphenyl ether as a yellow precipitate. Yield 0.08 g (1.08%). M.p. 156 – 158°.

Found %: C 65.28, 64.90; H 4.91, 4.86; N 4.25, 4.29. $C_{17}H_{15}O_5N$. Calculated %: C 65.25; H 4.80; N 4.48.

4. 5-Bromovanillin (VI). 5-Bromovanillin was obtained in nearly quantitative yield by the bromination of vanillin with dioxane dibromide [2]. M. p. 163-164° (from alcohol).

5. 5-bromoveratraldehyde (VII). 5-Bromoveratraldehyde was obtained by the methylation of 5-bromovanillin with dimethyl sulfate [3]. Yield 89.9%. M. p. 65-66° (from alcohol), b. p. 148-149° (3 mm).

6. 5-Bromoveratryl alcohol [4] (IX). To a solution of 15 g of 5-bromoveratraldehyde in 93 ml of methyl alcohol and 15 ml of formalin (d 1.093) was added with stirring 19.5 g of KOH in 16 ml of water in 10-15 minutes, not permitting the temperature to rise above 50°. When all the alkali had been added the reaction mass was heated for 20 minutes at 60-70° and for 3 hours at boiling. The residue after distilling off the solvent in vacuo was diluted with 50 ml of water, followed by extraction with ether (3 times with 100 ml portions). The extract

was dried over sodium sulfate, the ether removed, and the obtained bromoveratryl alcohol distilled. B. p. 163.5-164° (3.5 mm), 160-161° (2 mm), 177-178° (9 mm), $n^{19}D$ 1.5673. Yield 8.23 g (54.5%). Neutralization of the alkaline mother liquor with dilute (1 : 1) hydrochloric acid gave 5-bromovanillin. M. p. 161-163°, Yield 6.2 g (41%).

7. 3,4-Dimethoxy-5-bromobenzyl chloride (XI). Thionyl chloride (13.1 g) was added in drops (15 minutes) to 7.8 g of 5-bromoveratryl alcohol; the reaction mass was standing at room temperature for 1 hour. The excess thionyl chloride was vacuum-distilled, while the residue was neutralized with saturated aqueous sodium bicarbonate solution and the obtained 5-bromoveratryl chloride separated. Yield 8.3 g (99%). M. p. 56-58° (from petroleum ether [4]).

8. 3,4-Dimethoxy-5-bromobenzyl cyanide (XII). A solution of 13 g of sodium cyanide in 29 ml of water and 35 ml of alcohol was added to 8.3 g of 5-bromoveratryl chloride. The reaction mass was heated for 2 hours under reflux with stirring. The alcohol was vacuum-distilled, while the oily residue was extracted with ether (3 times with 20 ml portions). The extract was dried over sodium sulfate, the solvent removed, and the residue distilled to give 3,4-dimethoxy-5-bromobenzyl cyanide as a colorless crystalline substance. Yield 4.85 g (59.6%). B. p. 175-178° (3 mm), m. p. 64-65° [from a mixture of benzene and ligroine (1 : 1) or from carbon tetrachloride].

Found %: C 47.20, 47.15; H 4.21, 4.25; N 5.14. $C_{10}H_{10}O_2NBr$. Calculated%: C 46.9; H 3.93; N 5.47.

SUMMARY

2,3-Dimethoxy-5-cyanomethyl-4'-carboxydiphenyl ether, an intermediate in the synthesis of the ethers curarine and isochondodendrine, was obtained by a series of steps.

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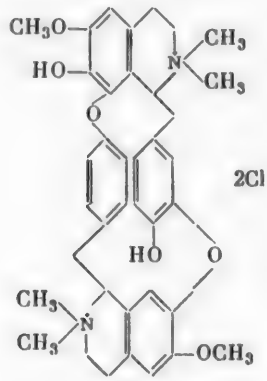
SYNTHESIS OF CURARE ALKALOIDS

SYNTHESIS OF 2-HYDROXY-3-METHOXY-5-(β-NITROVINYL)-4'-CARBOXYDIPHENYL ETHER

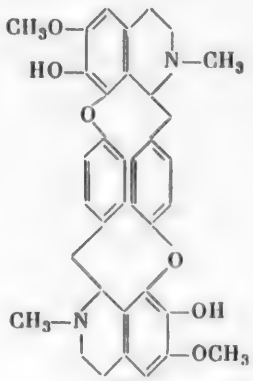
Yu. S. Tsizin, O. N. Tolkachev, L. V. Volkova, and N. A. Preobrazhenskii

Lomonosov Institute of Fine Chemical Technology (Moscow).

As can be seen from the formulas for tubocurarine (I) and isochondodendrine (II), the main representatives of tube curare, that part of the molecule having two oxygen-containing substituents attached through the diphenyl ether linkage is common to alkaloids of this series. Synthesis of such diphenylethers using the Ullmann condensa-



(I)



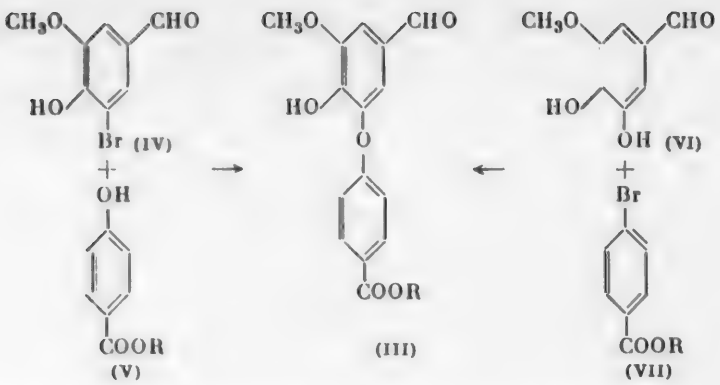
(II)

tion usually goes with low yields, especially if labile groupings are present [1].

The preparation of such diphenyl ethers, containing free phenolic hydroxyls, is not described in the literature. As is known, the synthesis of even the simplest hydroxyl-containing ethers goes with very low yields [2]. In view of this, developing methods for the preparation of such compounds is of great interest.

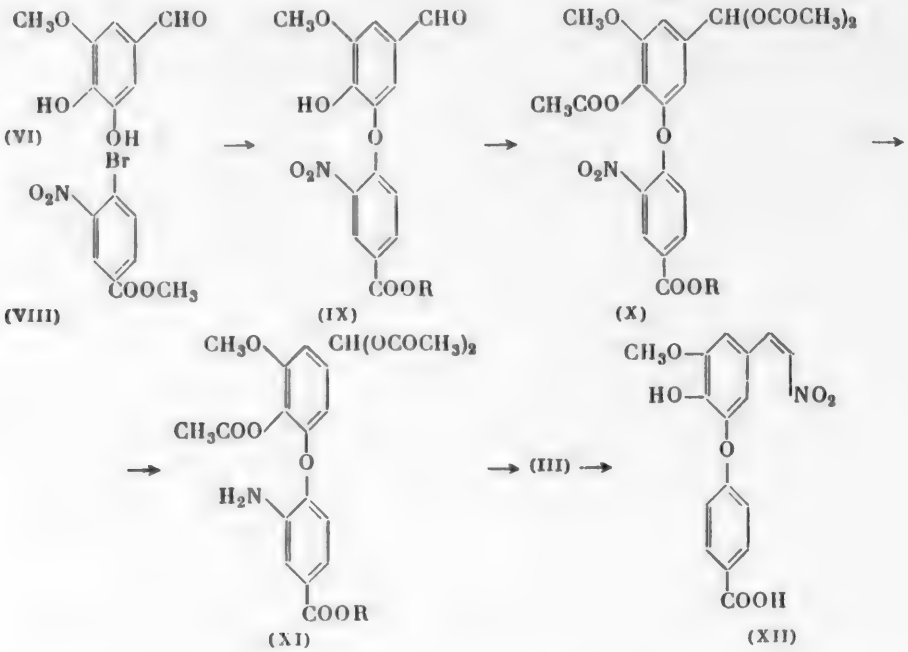
We obtained 2-hydroxy-3-methoxy-5-formyl-4'-carboxydiphenyl ether (III, R = H), the principal intermediate in the synthesis of 2-hydroxy-3-methoxy-5-(β-nitrovinyl)-4'-carboxydiphenyl ether (XII), by two routes: a) condensation of 5-bromovanillin (IV) with either the methyl or ethyl ester of 4-hydroxybenzoic acid (V, R = CH_3 or C_2H_5), and b) condensation of 3-methylgallaldehyde (VI) with the methyl ester of 4-bromobenzoic acid (VII).

The same substance is formed in both cases, which indicates that the phenolic hydroxyl groups in 3-methylgallaldehyde (VI) differ in their reactivity. It is interesting to mention that when (III) is prepared by reacting the ester of 4-hydroxybenzoic acid with (IV) it is necessary to use the ethyl ester, since when the reaction is run with the methyl ester the yield of desired product is decreased, due to the formation of a substantial amount of anisic acid and of its methyl ester with m. p. 48-49°.



To improve on the yield of compound (III) we worked out a new synthesis route.

Reaction of methyl 3-nitro-4-bromobenzoate (VIII) with (VI) gave us 2-hydroxy-3-methoxy-5-formyl-2,-nitro-4'-carboxydiphenyl ether (IX, R = H) and its methyl ester (IXb, R = CH_3). Compound (IXb) was converted to the triacetate (X), the nitro group was reduced catalytically with Raney nickel, and then the amino group



of compound (XI) was removed by reduction of the corresponding diazonium salt with hypophosphorous acid. Reaction of 2-hydroxy-3-methoxy-5-formyl-4'-carboxydiphenyl ether (III, R = H) with nitromethane converted it to 2-hydroxy-3-methoxy-5-(β-nitrovinyl)-4'-carboxydiphenyl ether (XII).

EXPERIMENTAL

1. 2-Hydroxy-3-methoxy-5-formyl-2'-nitro-4'-carbomethoxydiphenyl ether (IX, R = CH_3). A mixture of 4.6 g of 3-methylgallaldehyde [3], 7.1 g of methyl 3-nitro-4-bromobenzoate [4] and 35 ml of pyridine was heated for 1 hour at 120-125° (in a bath). Then the reaction was cooled, poured into 200 ml of water, neutralized with dilute (1 : 3) hydrochloric acid (to Congo), and extracted with ether (4 times with 60 ml portions). The extract, after washing with saturated sodium bicarbonate solution (50 ml), was dried over sodium sulfate.

Removal of the either in vacuo gave 2-hydroxy-3-methoxy-5-formyl-2'-nitro-4'-carbomethoxydiphenyl ether (IX, R = CH_3). Yield 2.1 g (22.1%). M. p. 149-152° (from methyl alcohol).

Found %: C 55.5; H 3.53; N 4.26. $C_{16}H_{13}O_8N$. Calculated %: C 55.4; H 3.74; N 4.03.

Triacetate (X, R = CH_3). M. p. 172-175° (from alcohol).

Found %: C 54.0; H 3.86; N 2.84. $C_{22}H_{21}O_{12}N$. Calculated %: C 53.8; H 4.27; N 2.85.

Evaporation of the methanolic mother liquors from the recrystallization of 2-hydroxy-3-methoxy-5-formyl-2'-nitro-4'-carbomethoxydiphenyl ether and reprecipitation of the residue from alkaline solution gave 2-hydroxy-3-methoxy-5-formyl-2'-nitro-4'-carboxydiphenyl ether (IX, R = H). Yield 1.4 g (15.35%). M. p. 207-210°. As a result, the total yield of (IX) was 37.45%.

Found %: C 53.78; H 3.25; N 4.36. $C_{15}H_{11}O_8N$. Calculated %: C 54.0; H 9.3; N 4.2.

Triacetate (X, R = H). Yield 56%. M. p. 196-198° (from methyl alcohol).

Found %: N 2.96. $C_{21}H_{19}O_{12}N$. Calculated %: N 2.93.

2. 2-Hydroxy-3-methoxy-5-formyl-4'-carboxydiphenyl ether (III, R = H). a) A solution of 3.5 g of 2-hydroxy-3-methoxy-5-formyl-2'-nitro-4'-carboxydiphenyl ether triacetate (X, R = H) in 75 ml of ethyl acetate was hydrogenated in the presence of 4 g of Raney nickel at 50° for 2 hours. The hydrogen absorbed was 495 ml (calculated 493 ml). The catalyst was filtered and washed with 50 ml of ethyl acetate. The solvent was removed in vacuo (30°), the residue treated with a mixture of 12 ml of glacial acetic acid and 10 ml of hydrochloric acid (d 1.19), cooled to 0°, and treated with a solution of 0.7 g of sodium nitrite in 3 ml of water. After 20 minutes a solution of hypophosphorous acid (obtained from 15 g of sodium hypophosphite, cooled to 0°, was added in 3 minutes, and the whole allowed to stand at +3° for 14 hours. After adding 135 ml of water the substance was extracted with ether (4 times with 60 ml portions). The extract was washed with water (twice with 50 ml portions), and then with 1N NaOH solution (15 ml), the acidification of which with dilute (1: 1) hydrochloric acid gave the diphenyl ether as precipitate. Yield 1.25 g (56.5%). M.p. 248.5 – 249° (from methyl alcohol).

Found %: C 62.87, 62.57; H 3.91, 4.14. $C_{15}H_{12}O_6$. Calculated %: C 62.50; H 4.17.

b) A mixture of 2.56 g of methyl 4-bromobenzoate (VII), 2.00 g of 3-methylgallaldehyde (VI), 1.56 g of anhydrous potassium carbonate, 0.14 ml of pyridine and 2.8 g of copper powder was heated in a nitrogen stream at 160-170° for 15 minutes, at 180-190° for 45 minutes, and at 190-200° for 30 minutes. The cooled reaction mass was treated with a solution of 6 g of NaOH in 60 ml of water, filtered, and extracted with ether (3 times with 50 ml portions). The alkaline solution was neutralized with dilute (1 : 1) hydrochloric acid and the obtained precipitate was extracted with ether (5 times with 50 ml portions). The ether extract was first dried over sodium sulfate and then evaporated. The residue (1.7 g) was saponified by heating under reflux for 1 hour with a solution of 5 g of NaOH in 50 ml of water, then diluted with 30 ml of water, neutralized with dilute (1 : 1) hydrochloric acid (to litmus), and the tarry precipitate separated. Again hydrochloric acid was added (to Congo), and the obtained precipitate was separated and washed with 30 ml of water. Repeated recrystallization from methyl alcohol gave a colorless crystalline substance. Yield 0.01 g (0.29%). M. p. 248-250°. The mixed melting point with the substance obtained in the preceding experiment was not depressed.

c) Potassium hydroxide (1.67 g), 7.2 g of ethyl 4-hydroxybenzoate (V, R = C_2H_5) and 5 g of 5-bromovanillin (IV) were successively dissolved in 20 ml of anhydrous alcohol. After adding 5 g of copper catalyst the alcohol was vacuum distilled, while the residue was heated for 1.5 hours with stirring in a nitrogen stream at 200 – 210°. The reaction mass was ground and then heated for 1.5 hours with a solution of 12 g of NaOH in 50 ml of water, after which the reaction mixture was filtered and acidified with 50 ml of hydrochloric acid (d 1.19). The obtained precipitate was separated and digested with ether (130 ml), which after solvent removal gave an oily substance that crystallized when rubbed with acetone. Yield of 2-hydroxy-3-methoxy-5-formyl-4'-carboxydiphenyl ether (III, R = H) 1.08 g (9.02%). M.p. 251.5 – 252.5° (from methyl alcohol).

Found %: C 62.62, 62.64; H 4.02, 4.21. $C_{15}H_{12}O_6$. Calculated %: C 62.5; H 4.17.

When the reaction was run in the presence of potassium carbonate, copper, and pyridine, the yield was 0.25%. M. p. 250-252° (from alcohol).

The 4'-methyl ester (III, R = CH_3) was obtained by conventional esterification. M. p. 110-112° (from a mixture of methyl alcohol and water, 1 : 1).

Found %: C 63.67, 63.58; H 4.45, 4.52. $C_{16}H_{14}O_6$. Calculated %: C 63.6; H 4.67.

3. 2-Hydroxy-3-methoxy-5-(β-nitrovinyl)-4'-carboxydiphenyl ether (XII). A mixture of 0.3 g of 2-hydroxy-3-methoxy-5-formyl-4'-carboxydiphenyl ether, 0.3 g of nitromethane, 0.02 g of methylamine hydrochloride, 0.02 g of sodium carbonate and 4 ml of methyl alcohol was heated under reflux until all of the precipitate went into solution (1.5 hours), after which it was allowed to stand at room temperature for a day, and here a crystalline precipitate deposited from solution. The reaction mass was concentrated to half of the original volume, followed by filtration of the nitrostyrene. Yield 0.25 g (70.0%). M. p. 210-210.5° (from methyl alcohol).

Found %: C 54.80; H 4.20; N 4.25, 4.37. $C_{18}H_{13}O_7N$. Calculated %: C 54.70; H 3.95; N 4.25.

SUMMARY

A number of new diphenyl ethers were obtained, being intermediates in the synthesis of tube curare alkaloids.

It was shown that it is possible to obtain diphenyl ethers by Ullmann condensation without protecting phenolic hydroxyls.

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MECHANISM OF THE ARBUZOV REARRANGEMENT*

A. I. Razumov

Kazan Chemical Technological Institute

Interest in the Arbuzov rearrangement, discovered more than 50 years ago [1], has never weakened. If in the first 40 years it attracted attention mainly as a fruitful and convenient way of obtaining various phosphorus-containing compounds, then in the last ten years much attention has been given to its mechanism.

The general scheme for the mechanism of the Arbuzov rearrangement [1, 2] was given by A. E. Arbuzov as follows:

$$1)\quad (RO)_3P + R'X \longrightarrow (RO)_3P\begin{matrix}\diagup R' \\ \diagdown X\end{matrix}$$

$$2)\quad (RO)_3P\begin{matrix}\diagup R' \\ \diagdown X\end{matrix} \longrightarrow R'{-}P(O)(OR)_2 + RX$$

As can be seen, the basic principle of the rearrangement is the conversion of esters of trivalent phosphorus to a compound with pentavalent phosphorus, having the phosphorus-carbon bond. One of the best chemical proofs that intermediate products are formed in the rearrangement is their isolation; also, that they can be decomposed further in accordance with the 2nd phase of the rearrangement.

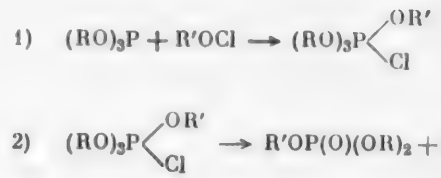
However, it should be mentioned that isolation of the intermediate addition products proves possible only in isolated rare cases [1, 3-5]. That intermediate products are formed when phosphites are reacted with alkyl halides also finds proof in some recent studies made of the Arbuzov rearrangement using physical methods [6, 7].

The mechanism scheme proposed by A. E. Arbuzov finds reliable confirmation at the present time by both chemical and physical methods. However, other concepts as to the mechanism of the rearrangement have appeared in recent years. So-called "anomalous" cases of the rearrangement have been described and various mechanisms have been proposed for them [8-16]. Also a radical chain mechanism has been proposed [17-22]. As regards the chain mechanism, only a single case is known where it was shown that reaction is of the radical type, which is not contrary to the general mechanism scheme of A. E. Arbuzov, and the intermediate product was isolated from the reaction [23]. As regards the other cases mentioned [17-22], then they can be considered as being possible and even somewhat probable, but not as proven facts.

It is much more interesting to discuss the so-called "anomalous" cases of the rearrangement, described in detail and studied mostly for cases involving the reaction of phosphites with α-haloaldehydes, α-haloketones and some other α-halocarbonyl compounds [8-16]. Compounds with pentavalent phosphorus are also usually obtained as a result of the mentioned reactions, but they lack the phosphorus-carbon bond (esters of phosphoric acid). Although in some cases, which are very important, compounds with the phosphorus-carbon bond (derivatives of phosphonic acids) are also formed simultaneously with the esters of phosphoric acid [10,21].

* Presented at the Training Session of the Chemical Institute of the Academy of Sciences of the USSR, September 27, 1957 (Kazan).

The formation of esters of phosphoric acid as the end products of the rearrangement of phosphites led to the creation of concepts of "anomalous" rearrangement products and "anomalous" cases of the rearrangement. Various mechanisms were proposed to explain this. However, in our opinion, it is more correct to consider phosphoric acid esters as the normal products of the Arbuzov rearrangement. The studies describing the rearrangement of phosphites with alkyl hypochlorites, alkanesulfenyl chlorides and chloramines [24, 25] serve as a good example on this score. Here the reactions go typically by the A. E. Arbuzov scheme with the formation of intermediate products, while the end products of the rearrangement are phosphoric acid esters. There can be no other products by the Arbuzov rearrangement scheme.



There is also no basis to consider phosphoric acid esters as "anomalous" products in the rearrangement of phosphites with α-halocarbonyl compounds. It is necessary to expand our concepts regarding the end products of the Arbuzov rearrangement, considering normal products to be not only compounds with the phosphorus-carbon bond, but also phosphoric acid esters. Our concepts regarding the Arbuzov rearrangement should also be expanded relative to certain other aspects. If previously it had been assumed that phosphites are capable of entering into the rearrangement only with compounds having labile halide [1, 2], then in recent years it has been shown that phosphites enter into the rearrangement also with a number of compounds not having labile halide; esters of toluenesulfonic acid [26], disulfides [27], saturated and unsaturated aldehydes [28, 29], and certain other compounds. In all of the cases discussed, either compounds with the phosphorus-carbon bond or phosphoric acid esters are obtained as a result of the rearrangement. Explanation for the reaction going toward the formation of either of the indicated products can be found in the electronic structure of the reagent taken. It is most probable that the direction of the reaction will depend on the degree of polarization, and also on the character and degree of conjugation shown by the chemical bonds of the reagent taken for rearrangement with phosphite.

However, the rate and even the very possibility of rearrangement depend not only on the nature of the reagent taken for rearrangement with phosphite, but also on the structure of the phosphite itself. Even in the early studies of A. E. Arbuzov [1] it was shown that the ethyl ester of phenylphosphonous acid rearranges 5 times as fast as does triethyl phosphite, while the ethyl ester of diphenylphosphonous acid rearranges 13 times as fast [1].

Expt. No.	Composition of mixture	Expt. temperature	Conversion time (in mm)	Temperature coefficient	Time required for 100% conversion reduced to 100° (in min)
1	$(C_2H_5O)_3P + C_2H_5I$ (obtained in presence of amine)	100.4° 110	1185 650	1.87	1214
2	$C_2H_5P(OC_2H_5)_2 + C_2H_5I$	64.5 72.1	540 240	2.90	12
3	$(C_2H_5)_2POC_2H_5 + C_2H_5I$	45 55	345 120	2.87	1

We studied the rearrangement rate using the ethyl ester of phosphorous acid and the ethyl esters of ethyl- and diethylphosphonous acids. Our measurement results, given in the table, clearly show the large influence exerted on the rearrangement rate of esters of trivalent phosphorus each time the ethoxyl group is replaced by ethyl.

The reason for esters of trivalent phosphorus showing a variable rearrangement rate remained obscure, and here A.E. Arbuzov wrote: "... . For the time being we must limit ourselves here either to simply stating the fact that the rate of the reaction is affected by different conditions or else attempt to relate separate facts by analogy." [1]

However, as early as 1952 we expressed an opinion as to the reasons for esters of trivalent phosphorus showing a variable rearrangement rate [30]. In our opinion, this is due to the presence of an unshared pair of electrons for trivalent phosphorus and the character of the substituents linked to phosphorus.

Compounds with trivalent phosphorus will be less inclined to addition reactions as the substituents show a larger negative and a smaller positive induction effect. For this reason it is natural that the inclination of P^3 for addition reactions should decrease in the order: $R_3P > R_2POR > RP(OR)_2 > P(OR)_3$.

The experiments described above serve to support this, as also do some later studies of a number of authors. It was shown that 2,2,2-trichlorotriethyl phosphite is incapable of rearrangement, or at most it does so with extreme difficulty [31]. From this viewpoint, a no less interesting case is the established fact that trifluorotrimethylphosphine is incapable of addition reactions [32].

The discussed literature data, and to a certain degree also our own experiments, permit making the following statements regarding the Arbuzov rearrangement.

1. Under the influence of compounds with labile halide, and also other electrophilic reagents, esters of trivalent phosphorus are capable of migrating to compounds with pentavalent phosphorus.

2. The migration goes with the formation of intermediate products.

3. The result of the rearrangement will be compounds either with the P–C bond (derivatives of phosphonic acids or phosphine oxides), or without the P–C bond (derivatives of phosphoric acid), or both types jointly.

4. Which of the indicated products is formed will probably depend on the degree of polarization, and also on the character and degree of conjugation shown by the chemical bonds of the reagent taken for reaction with the esters of trivalent phosphorus.

The structure of the trivalent phosphorus esters will exert substantial influence both on the rate and on the very possibility of rearrangement. One of the determining structural factors of the esters will be the influence exerted by phosphorus substituents on its unshared pair of electrons.

EXPERIMENTAL

To study the rearrangement rate we took the esters with the following constants:

$(C_2H_5O)_3P$ (obtained via the alcoholate), b. p. 46-46.5° (11 mm), d^{20}_4 0.9686, $n^{20}D$ 1.4125, MR_D 42.68; calc. 42.97.

$(C_2H_5O)_3P$ (obtained in the presence of amine), b. p. 45-46° (9 mm), d^{20}_4 0.9693, $n^{20}D$ 1.4130; MR_D 42.71; calc 42.97.

$C_2H_5P(OC_2H_5)_2$ b. p. 35.5-36.5° (10 mm), d^{20} 0.9065 $n^{20}D$ 1.4230, MR_D 42.12; calc. 42.03.

$(C_2H_5)_2POC_2H_5$, b. p. 69-71° (100 mm), d^{20}_4 0.8472, $n^{20}D$ 1.4360, MR_D 41.36; calc. 41.09.

All of the esters used to study the rearrangement rate were prepared in the presence of an organic base (amines). Triethyl phosphite, obtained via the alcoholate, is isomerized in 5 hours and 40 minutes at 110° (toluene vapors). According to A. E. Arbuzov the time is 6 hours. Triethyl phosphite, obtained in the presence of amine, isomerized nearly half as fast at 110° (10 hours and 50 minutes).

To study the rearrangement rate we used a dilatometer of essentially the same type as that used by A. E. Arbuzov [1]. Only the upper portion of the apparatus was changed, and here a side opening for the reflux condenser was attached. In this way the condensate descended along the inner wall of the dilatometer. The thermometer was graduated in 0.1°. The esters and alkyl halide were taken in an equimolar ratio.

The ester was weighed out in a tiny ground glass stoppered flask, and then the required amount of alkyl halide was added with a very fine pipette. The latter, through necessity, was always taken in one drop excess

(0.02-0.03 g). The weighed liquids were mixed in the flask and then transferred to the dilatometer. The latter was then placed in the vapors of the boiling liquid, used for thermostatting. The liquids used for the thermostatting were first dried and fractionally distilled. The fraction boiling at theright point was collected. The change in the reaction rate was followed by the decrease in the volume of liquid in the narrow neck of the dilatometer, behind which was placed a scale with 0.1° divisions. The readings were made at set brief time intervals. The end of reaction was assumed to be the point at which the volume of the liquid did not change in 2 hours. The obtained curves are not given here, since they could not be plotted for the ester of diethylphosphonous acid. Crystalline intermediate products are formed in the isomerization of the latter, which prevent following the volume change of the liquid in the narrow neck of the dilatometer. For this reason only the reaction end point was determined for this ester.

The results of our observations are summarized in the table.

SUMMARY

1. The rearrangement rate of the ethyl esters of phosphorous, ethyl - and diethylphosphonous acids was studied. Here it was shown that each replacement of the ethoxy group by ethyl increases the rearrangement rate substantially. An elucidation of the reasons for a variable rearrangement rate was offered.

2. It was shown that traces of amine in triethyl phosphite retard its rearrangement rate.

3. Based on a critical examination of literature data, as well as of our own experiments, we have presented a broader concept of the Arbuzov rearrangement.

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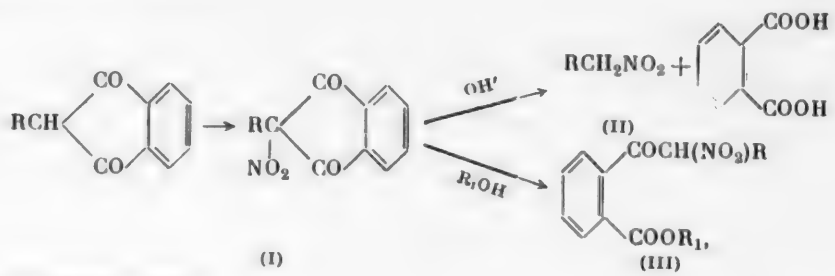
NITRATION OF PHTHALONES. II

L. Zalukaev and É. Vanag

Institute of Chemistry, Academy of Sciences of the Latvian SSR

In previous communications [1, 2] we described the nitration of phthalones and the hydrolytic cleavage of the nitration products by the scheme,

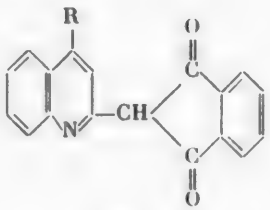


(I)

where R is heterocyclic.

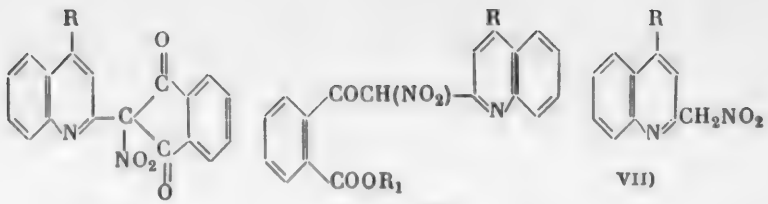
Nitrophthalones of type (I) were obtained from pyrophthalone, benzothiazophthalone, and from quinophthalone and its alkyl derivatives substituted in the aromatic ring. Alcoholysis gave esters of α-nitro-α-substituted acetophenone-o-carboxylic acid (III) in good yields, while hydrolysis gave nitromethanes with heterocyclic substituents (II).

In this paper we give the results obtained in the nitration of quinophthalones of general formula (IV), having alkyl substituents in the pyridine ring.



(IV)

It proved that, in this case also, the nitration goes very smoothly and under very mild conditions. The 2-nitro-2-substituted derivatives of 1,2-indandione obtained here, namely nitrophthalone (V), suffer smooth alcoholysis when simply heated in alcohols and form esters of α-nitro-α-alkylquinolyl-2-acetophenone-o-carboxylic acid (VI), in which the radical of the alkoxy group corresponds to the radical of the alcohol used. Treatment with aqueous sodium hydroxide solution leads to 2-nitromethyl-4-alkylquinoline (VII).



(V) (VI) VII)

EXPERIMENTAL

1. 4-Methylquinophthalone (IV, R = CH_3). A mixture of 84 g of 2,4-dimethylquinoline, 90 g of phthalic anhydride and several drops of tetrahydroquinoline was heated slightly more than 3 hours in an oil bath at 180-200°. The dark mass was allowed to cool, after which it was refluxed with alcohol, the precipitate filtered, and then washed with alcohol. The yield of finely crystalline product with m. p. 237-238° corresponds to that given in the literature for 4-methylquinophthalone [3]: 92 g (59%).

2. 2-Nitro-4'-methylquinophthalone (V, R = CH_3). Ten grams of 4-methylquinophthalone were covered with 75 ml of nitric acid (d 1.36). The mixture was cautiously heated on the water bath with vigorous shaking until all of the phthalone had dissolved and brown nitrogen oxides began to evolve. After this the mixture was poured into water and the nitration product, a slightly yellowish precipitate, was separated, washed with water, and dried. After two recrystallizations from acetone, m. p. 186-187°.

Found %: N 8.38. $C_{19}H_{12}O_4N_2$. Calculated %: N 8.43.

3. Esters of α-nitro-α-(4-methyl-2-quinolyl)acetophenone-o-carboxylic acid. a) Methyl ester (VI, R = R_1 = CH_3). The nitrophthalone was refluxed with methyl alcohol on the water bath, after which the suspension was cooled. The crystals of the ester were filtered. Orange-yellow compound with m. p. 193°. Recrystallization from methanol failed to change the melting point.

Found %: N 7.50. $C_{20}H_{16}O_5N_2$. Calculated %: N 7.69.

b) Ethyl ester (VI, R = CH_3; R_1 = C_2H_5). Obtained in a similar manner. Brown prisms with m. p. 157-158°.

Found %: N 7.31. $C_{21}H_{18}O_5N_2$. Calculated %: N 7.42.

4. 2-Nitromethyl-4-methylquinoline (VII, R = CH_3). 4-Methylquinophthalone (35 g) was covered with 200 ml of nitric acid (d 1.36), and then the flask was heated in warm water until the phthalone had dissolved and brown nitrogen oxides began to evolve. The precipitate obtained on pouring the mixture into cold water was washed with water, separated, and, while still moist, dissolved in 150 ml of 10% sodium hydroxide with vigorous shaking. Slight warming was resorted to in case of need. The solution was diluted with 150 ml of water, then filtered, and the filtrate acidified with dilute acetic acid. The precipitate crystallized after some standing, and then it was filtered, washed with water, and recrystallized from alcohol, m. p. 148-149°. Yield 24%. Several recrystallizations from alcohol raised the m. p. to 157-158°.

Found %: C 65.63; H 5.08; N 13.14. $C_{11}H_{10}O_2N_2$. Calculated %: C 65.34; H 4.95; N 13.87.

5. Denitromethylation of 2-nitromethyl-4-methylquinoline. 2-Nitromethyl-4-methylquinoline (8.5 g) was covered with 10 ml of benzoyl chloride. Heat was evolved here, and the substance dissolved. The dark solution was heated nearly to boiling for about another 10 minutes. The mixture on cooling began to crystallize at which point it was covered with alcohol and boiled. The precipitate was filtered. Weight 7.5 g, light yellow needles with m. p. 151-152° (from alcohol). Further purification failed to change the melting point.

The obtained product was covered with 25 ml of freshly prepared sodium ethylate, the sodium chloride filtered, the filtrate acidified, then extracted with ether, and the ether extract fractionated at atmospheric pressure. The fraction with b. p. around 220° gave a picrate with m. p. 210-211°, which corresponds to the picrate of lepidine. The mixed melting point with authentic product was not depressed.

6. 2-Nitro-4'-ethylquinophthalone (V, R = C_2H_5). Fourteen grams of finely pulverized 4-ethylquinophthalone (m. p. 197-198°, from glacial acetic acid, obtained in the same manner as the 4-methyl derivative) was covered with a mixture of 30 ml of nitric acid (d 1.48) and 75 ml of glacial acetic acid. The substance went into solution immediately, and after several seconds it was poured into water. The white curdy precipitate was filtered rapidly and washed well with water. The lustrous plates with a brownish tinge had m. p. 141-142° (decomp.) (from aqueous acetone). The crude product was used for further syntheses.

7. Esters of α-nitro-α-(4-ethyl-2-quinolyl)acetophenone-o-carboxylic acid. a) Methyl ester (VI, R = C_2H_5; $R_1 = CH_3$). The moist product obtained from the nitration of 4-ethylquinophthalone was refluxed with methanol for 3 hours. The solution was allowed to stand for a day, then filtered, and rubbing the side of the vessel with a glass rod gave a crystalline precipitate with m. p. 153°. Recrystallization from methanol gave the compound as light yellow plates with m. p. 176-177° (decomp.).

Found %: N 7.56. $C_{21}H_{18}O_5N_2$. Calculated %: N 7.41.

b) Ethyl ester (VI, R = $R_1 = C_2H_5$). Obtained in the same manner as the methyl ester, by refluxing the nitrophthalone with ethyl alcohol. Brown prisms with m. p. 146-147°

Found %: N 7.05. $C_{22}H_{20}O_5N_2$. Calculated %: N 7.14.

8. 2-Nitromethyl-4-ethylquinoline (VII, R = C_2H_5). Fourteen grams of crude nitroethylquinophthalone was dissolved in 150 ml of 10% sodium hydroxide. Both slight warming and vigorous shaking were employed. The light brown solution was diluted with an equal volume of water, filtered, and acidified with dilute acetic acid. The yellow precipitate was recrystallized from alcohol. Fractional crystallization gave three fractions of crystals that had the same external appearance: 1st, 1.25 g, m. p. 169-170°; 2nd, 1.70 g, m. p. 175-176°; 3rd, 1.50 g, m. p. 178°. The purest substance with m. p. 178° was taken for nitrogen analysis.

Found %: N 13.25. $C_{12}H_{12}O_2N_2$. Calculated %: N 12.96.

SUMMARY

The nitration of the phthalones of 4-methyl- and 4-ethylquinaldines was studied. Alcoholysis of the obtained α-nitrophthalones gave the corresponding esters of heterocyclic derivatives of α-nitro-acetophenone-o-carboxylic acid, while hydrolysis gave 2-nitromethyl-4-alkylquinolines.

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[2] L. P. Zalukaev and E. V. Vanag, J. Gen. Chem. 26, 2639 (1956);* 27, 3278 (1957).*

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* Original Russian pagination. See C. B. Translation.

POLYENE COMPOUNDS

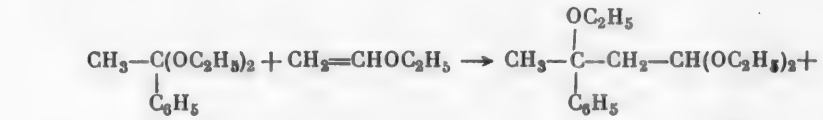
VII. CONDENSATION OF VINYL ETHYL ETHER WITH ACETALS OF AROMATIC ALDEHYDES AND KETONES

B. M. Mikhailov and G. S. Ter-Sarkisyan

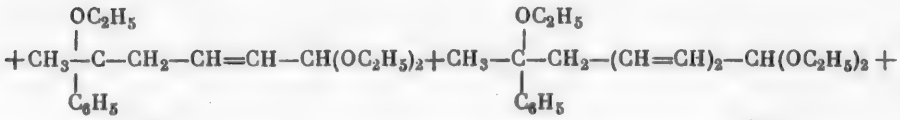
Institute of Organic Chemistry, Academy of Sciences of the USSR

As a rule, the reaction of acetals with vinyl ethers proceeds smoothly and leads to the formation of alkoxyalkanes. As had been shown earlier, reaction of the diethyl acetal of banzaldehyde [1] and of other cyclic aldehydes [2] with vinyl ethyl ether proceeds just as well as do analogous reactions in the aliphatic series, studied on a large number of examples [3, 4]. In contrast to acetals, the reaction of ketals with vinyl ethyl ethers has been studied to a much lesser extent [2, 5]. Together with this, studying the reaction of ketals with vinyl ethyl ether possesses interest as a technique for synthesizing various polyene compounds.

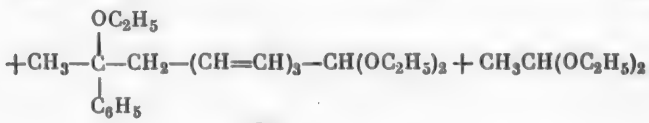
As the first example in the aliphatic aromatic ketone series we studied the reaction of acetophenone diethyl ketal with vinyl ethyl ether. It proved that this reaction is much more complex than the reaction of aromatic aldehyde acetals with, α, β-unsaturated ethers, and leads to the formation of a complex mixture of substances, from which we isolated the following compounds: 3-phenyl-1,1,3-triethoxybutane (I), 5-phenyl-1,1,5-triethoxy-2-hexene (II), 7-phenyl-1,1,7-triethoxy-2,4-octadiene (III), 9-phenyl-1,1,9-triethoxy-2,4,6-decatriene (IV) and acetaldehyde diethyl acetal.



(I)



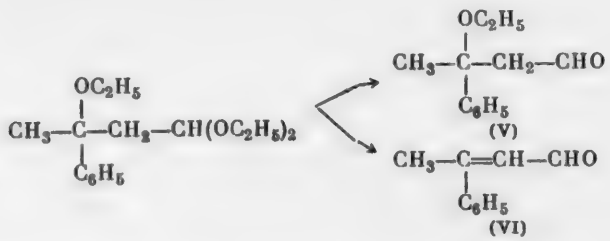
(II) (III)



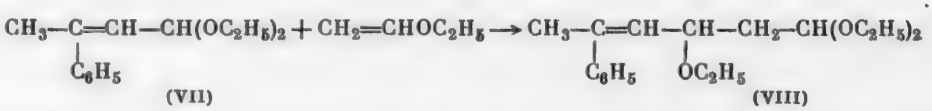
(IV)

When the reaction of acetophenone diethyl acetal with vinyl ethyl ether was studied under various conditions it was established that neither raising the temperature nor increasing the amount of acetal relative to the vinyl ethyl ether has much effect on the yield 3-phenyl-1,1,3-triethoxybutane. The best results were obtained using an equimolar ratio of the reactants, at 50°, in the presence of zinc chloride in acetic acid solution as catalyst.

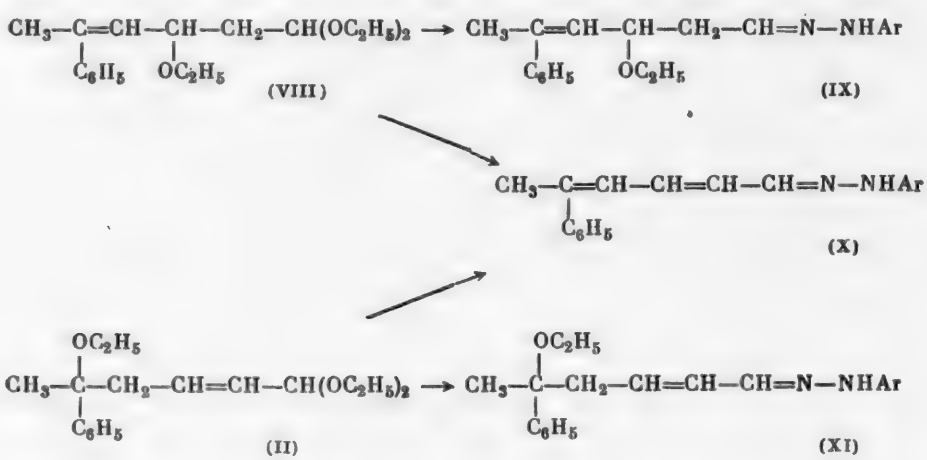
The structure of 3-phenyl-1,1,3-triethoxybutane (I) was shown by its saponification with dilute hydrochloric acid to 3-phenyl-3-ethoxy-butanal-1 (V), and under more drastic conditions, to β-methylcinnamaldehyde (VI).



To decide the structure of compound (II), being, according to the elementary analysis data, molecular weight and qualitative tests for the double bond, the acetal of an unsaturated aldehyde, it was first necessary to determine the position of the ethoxy group. For this purpose we synthesized β-methylcinnamaldehyde diethyl acetal (VII), reacted it with vinyl ethyl ether, and in this way synthesized 5-phenyl-1,1,3-triethoxy-4-hexene (VIII).

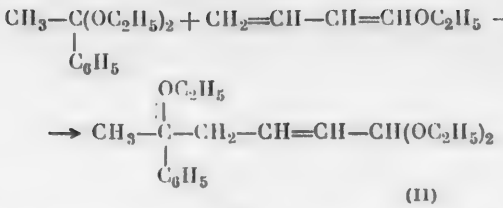


Compounds (II) and (VIII) were hydrolyzed and the thus obtained aldehydes were identified as the 2,4-dinitrophenylhydrazones. From compound (VIII) we obtained the 2,4-dinitrophenylhydrazone of 5-phenyl-3-ethoxy-4-hexenal (IX) and the 2,4-dinitrophenylhydrazone of 5-phenyl-2,4-hexadienal (X), whereas from compound (II) we obtained the 2,4-dinitrophenylhydrazone of 5-phenyl-5-ethoxy-2-hexenal (XI) and 2,4-dinitrophenylhydrazone (X). The indicated transformations are shown in the following schemes:



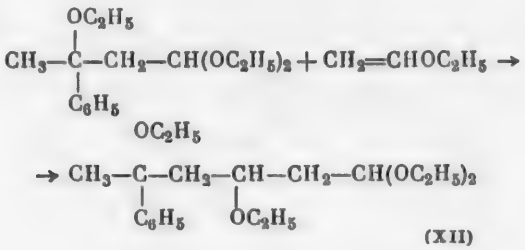
As a result, it was shown that the ethoxyl group in compound (II) is found, not on the third, but on the fifth carbon atom. Direct proof of the structure of (II) was accomplished by its direct synthesis from acetophenone diethyl acetal and 1-ethoxy-1,3-butadiene by the following scheme.

We isolated the 2,4-dinitrophenylhydrazone when the reaction product was saponified in the presence of 2,4-dinitrophenylhydrazine, which proved to be identical with 2,4-dinitrophenylhydrazone (XI).

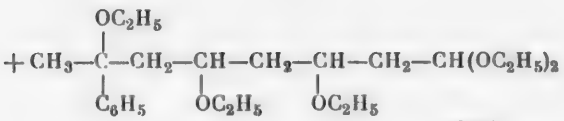


(II)

The formation of (II) when acetophenone diethyl acetal is reacted with vinyl ethyl ether apparently goes via condensation of the acetal with 1-ethoxy-1,3-butadiene, formed under the conditions of this reaction, and not via the successive addition of two molecules of vinyl ethyl ether to the acetal with subsequent cleavage of one molecule of alcohol. This postulation finds support in the fact that 5-phenyl-1,1,3,5-tetraethoxyhexane (XII) is obtained when 3-phenyl-1,1,3-triethoxybutane (I) is reacted with vinyl ethyl ether and compound (II) is not formed, i. e. compound (XII) does not cleave alcohol under the reaction conditions.



(XII)



(XIII)

The structure of the other two unsaturated aldehyde acetals, (III) and (IV), isolated by us from the reaction mixture obtained in the reaction of acetophenone diethyl acetal with vinyl ethyl ether, was not established by us specifically. According to the analysis data and molecular weight, each of these compounds has only one ethoxy group. The formation of 7-phenyl-1,1,7-triethoxy-2,4-octadiene (III) can be explained by the reaction of 5-phenyl-1,1,5-triethoxy-2-hexene (II) with vinyl ethyl ether and the subsequent cleavage of a molecule of alcohol. 9-Phenyl-1,1,9-triethoxy-2,4,6-decatriene (IV) can probably be formed by the reaction of 7-phenyl-1,1,7-triethoxy-2,4-octadiene (III) with one molecule of vinyl ethyl ether, as well as by the reaction of 5-phenyl-1,1, 5-triethoxy-2-hexene with a second molecule of 1-ethoxy-1,3-butadiene. In both cases it is the ethyl group located in series with the double bond that is cleaved. The alcohol thus formed reacts with ethyl vinyl ether, giving acetaldehyde diethyl acetal.

EXPERIMENTAL

Reaction of acetophenone diethyl ketal with vinyl ethyl ether. To a mixture of 194.26 g of acetophenone diethyl ketal and 0.26 ml of a 10% ether solution of boron trifluoride etherate, heated to 50°, was added dropwise, in 25 minutes, 72 g of vinyl ethyl ether, after which the reaction mixture was stirred for 15 minutes, the catalyst neutralized with solid sodium carbonate, and the stirring continued for another 3 hours at room temperature. Fractional distillation of the reaction mixture gave the following compounds.

1) Acetaldehyde acetal, 31.4 g (26.6%), b. p. 102-103°, $n^{20}D$ 1.3805; Literature data: B. p. 103.5°, $n^{20}D$ 1.3811 [6].

2) Original acetophenone diethyl ketal, 35.5 g, b. p. 89-92° (9 mm), $n^{19}D$ 1.4810.

3) 3-Phenyl-1,1,3-triethoxybutane (I), 41.5 g (15.6%).

B. p. 106-108° (1.5 mm), d^{20}_4 0.9713, $n^{20}D$ 1.4799, MR 77.89; calc. 77.41.

Found %: C 72.22; H 9.80. $C_{16}H_{26}O_3$. Calculated %: C 72.14; H 9.84.

4) 5-Phenyl-1,1,5-triethoxy-2-hexene (II), 5 g.

B. p. 132-133° (1 mm), d^{20}_4 0.9843, $n^{20}D$ 1.4940, MR 86.48; calc. 86.20.

Found %: C 73.45; H 9.62. M 293, 297. $C_{18}H_{28}O_3$. Calculated %: C 73.93; H 9.65. M 292.4.

5) 7-Phenyl-1,1,7-triethoxy-2,4-octadiene (III), 3.8 g.

B. p. 145-147° (1 mm), d^{20}_4 0.9937, $n^{20}D$ 1.5067, MR 95.45; calc. 94.78

Found %: C 75.58; H 9.14. $C_{20}H_{30}O_3$. Calculated %: C 75.43; H 9.50.

6) 9-Phenyl-1,1,9-triethoxy-2,4,6-decatriene (IV), 6.1 g.

B. p. 170-171° (1 mm), d^{20}_4 1.0267, $n^{20}D$ 1.5190. MR 102.3; calc. 103.7.

Found %: C 76.47; H 9.13. M 343.3, 342.2. $C_{22}H_{32}O_3$. Calculated %: C 76.69; H 9.37. M 344.4.

The residue from the first distillation (53.1 g) was a viscous tar.

When the same reaction was run in the presence of an acetic acid solution of zinc chloride the yield of 3-phenyl-1,1,3-triethoxybutane with b. p. 123-126° (3 mm) reached 34.0%.

Reaction of 3-phenyl-1,1,3-triethoxybutane (I) with vinyl ethyl ether. To a mixture of 53.2 g of 3-phenyl-1,1,3-triethoxybutane and 2 ml of a 10% acetic acid solution of zinc chloride, heated to 50°, was added 14.4 g of vinyl ethyl ether in 30 minutes. Then the mixture was kept at 50-51° for 2 hours, cooled to room temperature, and then shaken with 20 ml of 10% NaOH solution and 40 ml of diethyl ether. The ether layer was washed with water and then dried over sodium sulfate. Removal of the ether by distillation and 2 fractional distillations of the residue gave the following compounds.

1) Original 3-phenyl-1,1,3-triethoxybutane, 27.5 g, $n^{20}D$ 1.4775.

2) 5-Phenyl-1,1,3,5-tetraethoxyhexane (XII), 5.5 g (8.2%).

B. p. 147-149° (2 mm), d^{20}_4 0.9786, $n^{20}D$ 1.4736, MR 97.55; calc. 97.53.

Found %: C 71.16; H 9.92. $C_{20}H_{34}O_4$. Calculated %: C 71.00; H 10.03.

3) 7-Phenyl-1,1,3,5,7-pentaethoxyoctane (XIII), 3.5 g (4.3%).

B. p. 175-177° (2.5 mm), d^{20}_4 0.9915, $n^{20}D$ 1.4730.

Found %: C 69.66; H 10.03. $C_{24}H_{42}O_5$. Calculated %: C 70.20; H 10.31.

3-Phenyl-3-ethoxybutanal (V). A mixture of 10 g of 3-phenyl-1,1,3-triethoxybutane (I), 20 ml of ethyl alcohol and 10 ml of hydrochloric acid was heated to boiling, then cooled rapidly to room temperature, and poured into 50 ml of 10% sodium carbonate solution. The oil was extracted with ether, and the ether layer was washed with water and then dried. Removal of the ether and vacuum-distillation of the residue in a nitrogen gave 3.27 g (45.3%) of 3-phenyl-3-ethoxybutanal.

B. p. 130-133° (11.5 mm), d^{20}_4 1.0277, $n^{20}D$ 1.5170, MR 56.89; calc. 55.56.

Found %: C 75.40; H 8.36. $C_{12}H_{16}O$. Calculated %: C 75.20; H 8.39.

β-Methylcinnamaldehyde (VI). 3-Phenyl-1,1,-3-triethoxybutane (I) (75 g) was refluxed for 3 hours with 100 ml of glacial acetic acid and 10 g of sodium acetate in a nitrogen stream. The mixture after cooling to room temperature was treated with 250 g of ice and 100 g of crystalline sodium carbonate. The liberated aldehyde was extracted with either. The ether layer was washed, dried, and the ether distilled off. Distillation of the residue in vacuo gave 29.7 g (72.3%) of β-methycinnamaldehyde. B. p. 104 – 105° (3 mm), $n^{25}D$ 1.5870 [7].

2,4-Dinitrophenylhydrazone, m. p. 211° [7].

β-Methylcinnamaldehyde diethyl acetal (VII). A mixture of 10 g of β-methylcinnamaldehyde, 13.5 g of ethyl orthoformate, 5 ml of anhydrous alcohol and 0.25 g of anhydrous ammonium nitrate was kept for a day at room temperature. The next day the reaction mass was shaken with 20 ml of diethyl ether and 10 ml of 10% sodium carbonate solution. After conventional treatment the ether was distilled off, while the residue was vacuum-distilled. We obtained 10.6 g (70.3%) of β-methylcinnamaldehyde diethyl acetal.

B. p. 113-115° (3 mm), d^{20}_4 0.9746, $n^{20}D$ 1.5121.

Found %: C 76.20; H 8.85. $C_{14}O_{20}O_2$. Calculated %: C 76.33; H 9.15.

5-Phenyl-1,1,3-triethoxy-4-hexene (VIII). A mixture of 16.5 g of β-methylcinnamaldehyde and 0.75 ml of a 10% acetic acid solution of zinc chloride, heated to 50°, was treated with 5.4 g of vinyl ethyl ether at such a rate that the temperature did not exceed 50-51°. Then the mixture was held at 50-52° for 1 hour, cooled to room temperature, and then shaken with 25 ml of diethyl ether and 10 ml of 10% sodium hydroxide solution. After the usual treatment, the ether was distilled off and the residue was fractionated in vacuo to give 10.9 g (50%) of 5-phenyl-1,1,3-triethoxy-4-hexene.

B. p. 154-155° (3 mm), d^{20}_4 0.9688, $n^{20}D$ 1.4960, MR 86.19; calc. 87.16.

Found %: C 73.71; H 9.40. $C_{18}H_{28}O_3$. Calculated %: C 73.93; H 9.65.

2,4-Dinitrophenylhydrazones of 5-phenyl-3-ethoxy-4-hexenal and 5-phenyl-2,4-hexadienal, (IX) and (X). The addition of a solution of 0.5 g of 2,4-dinitrophenylhydrazine hydrochloride in a mixture of dioxane and alcohol (1 : 3) to an alcohol solution of 1 g of 5-phenyl-1,1,3-triethoxy-4-hexene (VIII) gave 0.2 g of a 2,4-dinitrophenylhydrazone with m. p. 90-106°, which after several recrystallizations from alcohol had m. p. 124-127° and was the 2,4-dinitrophenylhydrazone of 5-phenyl-3-ethoxy-4-hexenal (IX).

Found %: C 60.43; H 5.82. $C_{20}H_{22}O_5N_4$. Calculated %: C 60.24; H 5.61.

From the main mother liquor we isolated 0.1 g of a red crystalline precipitate with m. p. 175-212°, which after two recrystallizations from glacial acetic acid had m. p. 223-225° and was the 2,4-dinitrophenylhydrazone of 5-phenyl-2,4-hexadienal (X).

Found %: C 61.36; H 4.58; N 15.52. $C_{18}H_{16}O_4N_4$. Calculated %: C 61.36; H 4.58; N 15.91.

5-Phenyl-5-ethoxy-2-hexenal 2,4-dinitrophenylhydrazone (XI). Reaction of 2,4-dinitrophenylhydrazine with 1.7 g of 5-phenyl-1,1,5-triethoxy-2-hexene (II) under the conditions of the preceding experiment gave 1.6 g of the 2,4-dinitrophenylhydrazone, which after several recrystallizations from a 1 : 1 mixture of alcohol and glacial acetic acid gave 5-phenyl-5-ethoxy-2-hexenal 2,4-dinitrophenylhydrazone (XI) as orange-red plates with m. p. 146-148°.

Found %: C 60.23; H 5.56; N 14.29. $C_{20}H_{22}O_5N_4$. Calculated %: C 60.24; H 5.61; N 14.07.

From the mother liquor we isolated the 2,4-dinitrophenylhydrazone of 5-phenyl-2,4-hexadienal, which after several recrystallizations from glacial acetic acid had m. p. 223-224.5°, and did not depress the melting point when mixed with the specimen obtained in the preceding experiment.

Reaction of acetophenone diethyl ketal with 1-ethoxy-1,3-butadiene. A mixture of 47.53 g of acetophenone diethyl ketal and 0.5 ml of a 10% acetic acid solution of zinc chloride, heated to 50°, was treated in 25 minutes with 8 g of 1-ethoxy-1,3-butadiene [8]; then the mixture was kept at 50° for 1 hour, followed by treatment with 5% potassium carbonate in the same manner as described in previous experiments. Extraction of the reaction product with ether, followed by drying of the ether extract, removal of the ether by distillation, and vacuum distillation of the residue, gave 36.8 g of original ketal and 2.1 g of substance with b. p. 168-170° (7 mm).

A solution of 1 g of this substance in 5 ml of alcohol was mixed with an alcoholic hydrochloric acid solution of 2,4-dinitrophenylhydrazine. The obtained crystals were recrystallized 3 times from alcohol. We obtained 0.15 g of 5-phenyl-5-ethoxy-2-hexenal 2,4-dinitrophenylhydrazone with m. p. 146 – 148.5°. The mixed melting point with the specimen obtained in the preceding experiment was not depressed.

SUMMARY

1. It was established that the reaction of acetophenone diethyl ketal with vinyl ethyl ether yields the following compounds: 3-phenyl-1,1,3-triethoxybutane, 5-phenyl-1,1,5-triethoxy-2-hexene, 7-phenyl-1,1,7-triethoxy-2,4-octadiene, 9-phenyl-1,1,9-triethoxy-2,4,6-decatriene and acetaldehyde diethyl acetal.

2. It was found that the reaction of acetophenone diethyl ketal with 1-ethoxy-1,3-butadiene yields 5-phenyl-1,1,5-triethoxy-2-hexene.

3. The reaction of vinyl ethyl ether with the diethyl acetals of 3-phenyl-3-ethoxy-1-butanal and β-methylcinnamaldehyde was studied.

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ORGANOBORON COMPOUNDS

XXXVIII. REACTION OF TRIALKYLBORONS WITH SULFUR. SYNTHESIS OF ESTERS OF DIALKYLTHIOBORIC ACIDS

B. M. Mikhailov and Yu. N. Bubnov

Institute of Organic Chemistry, Academy of Sciences of the USSR

Trialkyl compounds of boron are oxidized by oxygen to give, depending on the conditions, either esters of dialkylboric or of alkylboric acids [1]. It seemed of interest to investigate the ability of trialkylborons to react with another Group 6 element, namely sulfur. Experiment revealed that heating either tri-n-propylboron or tri-n-butylboron with sulfur at 145° gave n-propyl di-n-propylthioborate (I, R = n-C_3H_7) and n-butyl di-n-butylthioborate (I, R = n-C_4H_9), respectively.

$$R_3B + S \longrightarrow \underset{(I)}{R_2BSR},$$

where R = n-C_3H_7, n-C_4H_9.

Here, by analogy with the oxidation of trialkylborons, the first to be formed is probably the molecular compound with sulfur, which then reacts with a second molecule of R_3B.

$$R_3B + S_n = R_3B \leftarrow S_n$$

$$R_3B \leftarrow S_n + R_3B = 2R_2BSR + S_{n-2}$$

Of the esters of dialkylthioboric acids only the methyl ester of dimethylthioboric acid is known up to now, obtained by reacting methyl mercaptan with either tetramethyldiborane [2] or dimethylboron bromide [3]. Long heating of this ester with methyl thioborate gave the dimethyl ester of methylthioboric acid [3].

The esters of dialkylthioboric acids are extremely reactive compounds. They are hydrolyzed by water to dialkylboric acids, while with alcohols they are converted to esters of dialkylboric acids. In this way the reaction of n-propyl di-n-propylthioborate with methyl alcohol gave methyl di-n-propylborate.

$$(n\text{-}C_3H_7)_2B\text{—}S\text{—}n\text{-}C_3H_7 + CH_3OH \longrightarrow (n\text{-}C_3H_7)_2B\text{—}O\text{—}CH_3 + n\text{-}C_3H_7SH$$

The esters of dialkylthioboric acids react with amines to yield N-substituted dialkylboron amines.

$$R_2B\text{—}S\text{—}R + NH_2R' \longrightarrow R_2BNHR' + RSH$$

Reaction of isobutylamine with the ester of di-n-propylthioboric acid gave di-n-propylisobutylaminoboron; reaction of the ester of di-n-butylthioboric acid with aniline gave di-n-butylanilinoboron.

The esters of dialkylthioboric acids are stable at high temperature. Thus, n-propyl di-n-propylthioborate fails to show disproportionation when heated at 160° for 4 hours.

EXPERIMENTAL

n-Propyl di-n-propylthioborate. Into a 3-necked flask, fitted with reflux condenser and nitrogen inlet tube, was charged 18.5 g of tri-n-propylboron (b. p. 42-44° at 7 mm) and 4.2 g of powdered sulfur. The mixture was heated with vigorous stirring in a metal bath at 180° (in the bath) until all of the sulfur had dissolved. Then the solution was heated at 140-145° for 3.5 hours. The reaction products were distilled from a Claisen flask, followed by fractionation through a Hempel column. We obtained 5.4 g of starting tri-n-propylboron and 8.6 g (38%) of n-propyl di-n-propylthioborate.

B. p. 77.5-78.5° (7 mm), $n^{20}D$ 1.4546, d^{20}_4 0.8241.

Found %: C 62.55; H 12.15; S 18.07; B 6.47. $C_9H_{21}SB$. Calculated %: C 62.79; H 12.32; S 18.63; B 6.28.

In addition, we obtained 4.0 g of a fraction with b. p. 106-112° (7 mm), which was not investigated.

n-Propyl di-n-propylthioborate is a colorless liquid with a very disagreeable odor, and suffers both oxidation and hydrolysis in the air; it is readily soluble in organic solvents.

n-Butyl di-n-butylthioborate. An experiment was run in the same manner as in the preceding. For reaction we took 54.5 g of tri-n-butylboron (b. p. 87 – 89° at 6 mm) and 9.6 g of sulfur. Fractional distillation of the reaction products gave 18.2 g of starting tri-n-butylboron and 25.8 g (40.3%) of n-butyl di-n-butylthioborate.

B. p. 117.5-118.5° (8 mm); $n^{20}D$ 1.4548; d^{20}_4 0.8367.

Found %: C 67.26; H 12.72; S 14.55; B 5.12. $C_{12}H_{27}SB$. Calculated %: C 67.27; H 12.71; S 14.97; B 5.05.

The 3rd fraction, weighing 3 g and with b. p. 127-136° (7 mm), was not investigated.

n-Butyl di-n-butylthioborate is a colorless liquid with a very disagreeable odor, and suffers both slow hydrolysis and oxidation in the air; it is readily soluble in organic solvents.

Methyl di-n-propylborate. A mixture of 7.9 g of n-propyl di-n-propylthioborate and 3.6 ml of anhydrous methyl alcohol was heated under reflux for 4 hours. Then the excess methyl alcohol and the propyl mercaptan were distilled at atmospheric pressure, while the residue was fractionated in vacuo. We obtained 3.1 g (52%) of methyl di-n-propylborate.

B. p. 55.5-56° (44 mm), $n^{20}D$ 1.4023, d^{20}_4 0.7729.

Found %: B 8.64. $C_7H_{17}OB$. Calculated %: B 8.45.

Di-n-propylisobutylaminoboron. To 11.4 g of n-propyl di-n-propylthioborate was added 4.5 ml of isobutylamine. Mixing of the reactants was accompanied by much evolution of heat. The solution was refluxed for 4 hours, after which the propyl mercaptan was distilled from the mixture of products, while the residue was fractionated. We obtained 8.8 g (79%) of di-n-propylisobutylaminoboron as a colorless liquid.

B. p. 65.7-66.3° (7 mm), $n^{20}D$ 1.4282, d^{20}_4 0.7724.

Found %: C 69.74; H 14.18; B 6.59. $C_{10}H_{24}BN$. Calculated %: C 71.01; H 14.30; B 6.40

Di-n-butylanilinoboron. Seven grams of n-butyl di-n-butylthioborate was mixed with 3.6 g of aniline, and here much evolution of heat was observed. The solution was heated for 2 hours at 140 – 150°. Then the n-butyl mercaptan was distilled off at atmospheric pressure (b. p. 98-99°), while the residue was fractionated in vacuo. We obtained 6.7 g (95%) of di-n-butylanilinoboron.

B. p. 138-139° (7.5 mm), $n^{20}D$ 1.5001, d^{20}_4 0.8808.

Found %: C 77.21; H 11.10; B 5.16. $C_{14}H_{24}NB$. Calculated %: C 77.43; H 11.14; B 4.98.

Di-n-butyanilinoboron is a colorless mobile liquid, slowly oxidizing in the air, and miscible in all proportions with most organic solvents.

SUMMARY

1. Trialkylborons react with sulfur at 145° to yield esters of dialkylthioboric acids.

2. The esters of dialkylthioboric acids when reacted with alcohols are converted to esters of dialkylboric acids; with amines the esters of dialkylthioboric acids react to yield N-substituted dialkylboron amines.

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THE TRANSFORMATION OF URIC ACID INTO 8-METHYLXANTHINE

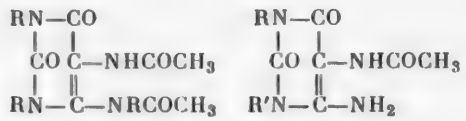
IV. HYDROLYSIS OF 4'5-BIS(ACETAMIDO)URACIL

E. S. Golovchinskaya and F. L. Kolodkin

S. Ordzhonikidze All-Union Chemical Pharmaceutical Research Institute

The methylation of 4,5-bis(acetamido)uracil (diacetate I) with 3 moles of dimethyl sulfate in aqueous alkali leads to the formation of the extremely water soluble 1,3-dimethyl-4-acetylmethylamino-5-acetamidouracil (II [1]. It was found by one of us [2] that toward the end of reaction the clear solutions obtained as the result of such methylation at times deposit crystalline precipitates that are difficultly soluble in water. This hardly happens when the diacetate is methylated, for it immediately crystallizes when the hot aqueous solution is cooled (fraction A). Therefore, the formation of the difficultly soluble precipitates must invariably occur in the methylation of the cyrstals that are isolated from the evaporated filtrates after the removal of fraction A (fraction b).

An investigation of the obtained precipitates revealed that they represent a mixture of two methylated derivatives of 4-amino-5-acetamidouracil (monoacetate III), and specifically, the 3-methylmonoacetate (IV) and the 1,3-dimethyl monoacetate (V).



(I) R = H.
(II) R = CH_3.

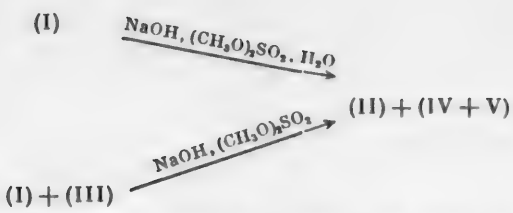
(III) R = R′ = H.
(IV) R = H, R′ = CH_3.
(V) R = R′ = CH_3.

The structure of (IV) and (V), supported by analysis, was established using a number of characteristic reactions: their conversion to the corresponding 8-methylxanthines (3-methyl- and 1,3-dimethyl-) by prolonged heating with acetic anhydride; quantitative cleavage of 1 mole of acetic acid when heated with dilute mineral acids; formation of crystalline perchlorates [3, 4] when reacted with 70% $HClO_4$, and finally, comparison with the specimens of (IV) and (V) synthesized from the corresponding 4,5-diaminouracils, used as intermediates in the synthesis of theobromine and theophylline.

Additional, even though indirect, proof that the crystalline precipitate isolated from the methylation reaction is a mixture of methylated monoacetates is found in the fact that heating the mixture with mineral acid yields 1,3,1', 3'-tetramethylhydurilic acid. The formation of this acid when 1,3-dimethyl-4,5-diaminouracil or its 5-acyl derivatives are reacted with sulfuric acid and the scheme proposed for this reaction have been described by Bredereck and coworkers [5].

Naturally the question arose as to the source of the formation of (IV) and (V), whether it was secondary hydrolysis during methylation of the diacetate (I), or whether it was methylation of monoacetate (III), present as impurity in the original diacetate (I).

Evidence in support of the second hypothesis was found in the fact that fraction A dissolves in hot 70% $HClO_4$ to give a solution that remains clear when strongly cooled, and also when seeded with the perchlorate of (III) [3]; in contrast to it, fraction B gives the crystalline perchlorate of (III) with comparative ease soon



after being dissolved in $HClO_4$, in which connection the amount of perchlorate crystals that deposits is always proportional to the extent of concentrating the aqueous filtrates. The filtered perchlorate is readily hydrolyzed with water, and the (III) that is obtained in this manner can be further characterized by its comparatively low solubility in boiling water (1 : 85), in which respect it differs from diacetate (I), soluble in water (1 : 30).

As a result, although the presence of monoacetate (III) as impurity in the original diacetate (I) can thus be considered firmly established, still it is necessary to explain its accumulation in the aqueous mother liquors. The failure of attempts made to isolate (III) as the prechlorate from the crude product obtained in the cleavage of uric acid with acetic anhydride, prior to its recrystallization from water, indicated that (III) is not formed in the cleavage of uric acid. The theory arose that the appearance of (III) is linked with the recrystallization of (I) from water and is due to its hydrolytic cleavage: (I) + $H_2O \rightarrow$ (III) + CH_3COOH. If this is true, then (III) should undoubtedly be formed when large volumes of water filtrates, containing (I), are evaporated.

The assumption that diacetate (I) is capable of being hydrolyzed by water in the absence of either acid or alkali is contradictory to the currently existing concepts regarding its chemical properties [6]. Nevertheless, long refluxing of a known weight of analytically pure (I) in 100 volumes of water confirmed the fact that a gradually retarded accumulation of acetic acid was taking place in the solution. The precipitate obtained on cooling the filtered solution proved, after recrystallization from water, to be monoacetate (III).

In addition, it was noticed that the refluxing solution gradually turned yellow, assumed a blue fluorescence, and after 15 hours began to deposit a yellow-green precipitate, insoluble in boiling water. Its amount after refluxing for 34 hours represented about 1.5% of the weight of original diacetate (I).

Study of the colored substance, isolated from the boiling solution, revealed that its UV spectrum in a solution of 0.1 N NaOH solution coincides quite well with the UV spectrum of a mixture of 3 parts of symmetrical and 1 part of unsymmetrical bis-alloxazines [7], described by Bredereck and coworkers [5] as being the transformation products of methylated 4,5-diaminouracils or their 5-acyl derivatives under the influence of acids (see Fig. 1).

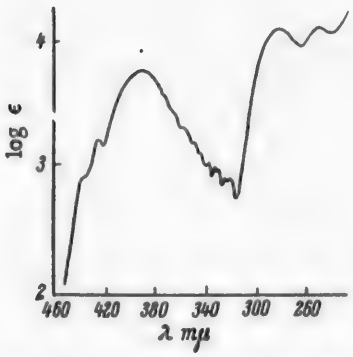


Fig. 1. Ultraviolet spectrum of hydrolysis product of 4,5-bis(acetamido)uracil (I).

Control experiments in which pure (III) was subjected to prolonged boiling with water revealed that neither liberation of acetic acid nor coloring of the solution occurs; consequently, the formation of the former as the result of heating (I) with water must be attributed solely to the conversion of diacetate (I) to monoacetate (III).

In the case where the acetic acid, formed as the hydrolusis of the diacetate with water progresses, is distilled off, it proves possible to collect and titrate 1 mole of CH_3COOH in the receiver. Here the formation of a precipitate insoluble in hot water is not observed, while the solution assumes only a very slightly yellow color. A solution of completely pure monoacetate remains in the reaction flask. Its further heating with dilute sulfuric acid makes it possible to quantitatively distill off also the second mole of acetic acid.

Earlier it had been shown by one of us [8] that the ability of the diacetate to cyclize with the formation of 8-methylxanthine when heated with either alkalies or acids is the reason why Biltz and Schmidt [4] were unable to saponify both of its acetyl groups. Now for the first time we were able to saponify the diacetates with a quantitative liberation of 2 moles of acetic acid by the technique of dividing the hydrolysis process into two steps, the first of which is run using neither acid nor alkali.

At the present time the prospect of synthesizing various derivatives of xanthine and isoxanthine from the intermediates formed in the transformation of uric acid into 8-methylxanthine when it is heated with acetic anhydride becomes quite real. The present study revealed that in those cases where the contemplated synthesis is based on further transformations of the diacetate (I) or of the triacetate, but not of the monoacetate, recrystallization of the original substance from water should be avoided, since this leads to losses; a good example of this is the substantial increase in the yield of methylisocaffeine that is obtained when the operation of recrystallizing the cleavage product of uric acid from water is eliminated [2].

EXPERIMENTAL

Preparation of mixed methylated monoacetates – 3-methyl - and 1,3-dimethyl-4-amino-5-acetamidouracils [2] (IV and V). a) A mixture of 150 g of uric acid, 600 ml of acetic anhydride and 150 ml of pyridine bases was refluxed for 4.5 hours, then washed with dichloroethane, the mixture of solids recrystallized from 4500 ml of water, the product filtered after cooling the hot water solution (weight of fraction A 80.9 g), the filtrate evaporated in vacuo to a volume of 700-800 ml, and then cooled. The product (fraction B, weight 38 g) obtained on cooling was methylated (150 ml of water, 64 ml of dimethyl sulfate and 44 ml of 42% NaOH solution, 30-35°, pH 6.7-6.8). The crystalline reaction mass obtained from the methylation of fraction B was filtered, and the 12.6 g of mixed product obtained here was recrystallized from 125 ml of water to give 9 g of substance with m. p. 276-279°.

b) After washing with dichloroethane, the mixture of solids (Expt. "a") was refluxed with 4500 ml of water for 5 minutes, the solution filtered while hot, the entire filtrate (without isolating fraction A) concentrated in vacuo to a volume of 500 ml, and the thus obtained suspension was methylated (192 ml of dimethyl sulfate, 132 ml of 42% NaOH solution, 30-35°, pH 6.7-6.8). At the end of methylation the reaction mass was filtered. The obtained crystals weighed 23 g and had m. p. 274-276°. Repeated recrystallization from water (1 : 20) raised the m. p. to 295° (decomp.); its mixture with the 3-methyl-4-amino-5-acetamidouracil (IV) obtained by the acetylation of 3-methyl-4,5-diaminouracil with glacial acetic acid had m. p. 295-297° (decomp.).

Found %: C 42.37; H 5.52; N 28.42. $C_7H_{10}O_3N_4$. Calculated %: C 42.42; H 5.55; N 28.28.

Transformation of 3-methyl-4-amino-5-acetamidouracil (IV) into 3,8-dimethylxanthine. Five grams of (IV) with m. p. 295° from Expt. "b" was refluxed for 30 hours with 50 ml of acetic anhydride. The solution on cooling deposited 3.4 g (75%) of crystals, which after recrystallization from 200 ml of water had m. p. 338-345°; the mixed m. p. with 3,8-dimethylxanthine was 338-345°.

Found %: N 30.89. $C_7H_8O_2N_4$. Calculated %: N 31.10.

A solution of 1 g of the obtained 3,8-dimethylxanthine in 5% NaOH was methylated at 20° with 2.5 ml of dimethyl sulfate. The reaction mass yielded 0.8 g of crystalline methylcaffeine with m. p. 209-211° (from water); the mixed m. p. with authentic methylcaffeine was 209-211°.

Second methylation of the substance crystallizing in the methylation of fraction B (preparation of 1,3-dimethyl-4-amino-5-acetamidouracil (V) and its transformation). A suspension of 9 g of substance "a" with m. p. 276-279° in 50 ml of water was methylated by the gradual simultaneous addition of 6.5 ml of dimethyl sulfate and 4 ml of 42% NaOH solution at 35° and pH 9; the reaction mass was cooled in ice, and the precipitate was filtered, washed with ice water, and dried. Weight 8 g, m. p. 265-270°, and after recrystallization from 75 ml of alcohol, weight 5 g, and m. p. 270-275° (melts with decomposition, after which it solidifies and melts again at 324°). After 3 recrystallizations from alcohol, m. p. 277-279° (decomp.); its mixture with the 1,3-dimethyl-4-amino-5-acetamidouracil obtained by the acetylation of 1,3-dimethyl-4,5-diaminouracil with glacial acetic acid had m. p. 277°.

Found %: N 26.32. $C_8H_{12}O_3N_4$. Calculated %: N 26.41.

A mixture of 0.8 g of the obtained substance (from 5.3 g) and 2 ml of 70% $HClO_4$ was heated on the water bath. On cooling in ice the clear solution crystallized, the crystals were filtered, washed with ether, dissolved in 15 ml of warm water, and the solution neutralized (methyl red indicator) with 0.1 N NaOH solution. The pure 1,3-dimethyl-4-amino-5-acetamidouracil (V), m. p. 278-279° (from alcohol), crystallized from the neutral aqueous solution on cooling.

Found %: N 26.63. $C_8H_{12}O_3N_4$. Calculated %: N 26.41.

Determination of acetyl group in (V). A sample of 0.1198 g of substance was boiled with 40 ml of 10% H_2SO_4, with simultaneous passage of steam and removal of formed acetic acid by distillation. Titration of the distillate required 5.62 ml of 0.1 N NaOH solution (99.4%). Calculated amount of 0.1 N NaOH is 5.65 ml.

Transformation of 1,3-dimethyl-4-amino-5-acetamidouracil (V) into 1,3,8-trimethylxanthine. a) Two grams of (V) was refluxed for 10 hours with 20 ml of acetic anhydride. The solution on cooling deposited 1 g of crystals with m. p. 324-326°. The acetic anhydride was distilled from the filtrate and another 0.4 g of substance was isolated, m. p. 323-326°. Yield 82%, and the mixed m. p. with 3,8-dimethylxanthine was 280-285°, while with 1,3,8-trimethylxanthine it was 324-326°. For analysis the substance was recrystallized from 50 ml of water.

Found %: C 49.61; H 4.94; N 28.99. $C_8H_{10}O_2N_4$. Calculated %: C 49.48; H 5.15; N 28.86.

b) One gram of (V) was heated in a crucible. The substance melted with stormy evolution of gas at 280°, and then solidified. Weight of melt 0.85 g, m. p. 325-327° (from water). Its mixture with the 1,3,8-trimethylxanthine obtained in Expt. "a" had m. p. 324-327°.

Results of Titrating Reaction Solution

Sample No.	Time of reflux (in hours)	Volume of sample to the initial (in %)	Amount of 0.1N NaOH solution consumed	Amount of CH_3COOH titrating with respect to one acetyl group (in %)
1	6	10	2.51	22
2	14	10	4.40	38.1
3	30	10	8.50	73.6
4	36 (34 hrs + 2 hrs for distilling off the water)	50	44.4	76.8

Transformation of mixture of 3-methyl-4-amino-5-acetamidouracil (IV) and 1,3-dimethyl-4-amino-5-acetamidouracil (V) into 1,3,1',3'-tetramethylhydurilic acid. Twenty grams of the substance that crystallized from the methylation reaction in Expt. "b" was methylated a second time, as described above, after which it was refluxed for 5 hours with 20 ml of hydrochloric acid (d 1.19). Cooling gave a small amount of coarse transparent rhombic crystals with m. p. 258-259° (from butyl alcohol). Its mixture with authentic 1,3,1', 3'-tetramethylhydurilic acid (synthesized from 1,3-dimethyl-4,5-diaminouracil [5] had m. p. 258-259°. *

Found %: C 46.53; H 4.57; N 18.11. $C_{12}H_{14}O_6N_4$. Calculated %: C 46.45; H 4.51; N 18.06.

Preparation of 4-amino-5-acetamidouracil (III) perchlorate. Fraction B (0.8 g) was dissolved with heating in 2 m. of 70% $HClO_4$. The cooled solution crystallized when seeded with the perchlorate of (III). The product was filtered and then treated with 0.1 N NaOH solution in the manner described above. We obtained 0.026 g of substance, the recrystallization of which require 2.2 ml of water. The crystals had the same appearance as monoacetate (III).

Found %: N 30.58. $C_6H_8O_3N_4$. Calculated %: N 30.43.

Hydrolysis of 4,5-bis(acetamido)uracil (I). a) A solution of 2.6095 g of pure diacetate (I) in 200 ml of preboiled distilled water was heated under reflux for 34 hours. Three samples (each 10% of the initial volume) were taken during this time and each was titrated with 0.1 N NaOH solution in the presence of methyl red.

* The authors wish to thank K. A. Chkhikvadze for kindly supplying the specimens of authentic 1,3,1',3'-tetramethylhydurilic acid, and also the 3-methyl- and 1,3-dimethyl-4,5-diaminouracils.

After 14 hours a fine yellow-green precipitate appeared in the boiling solution, the amount of which increased gradually.. After refluxing for 34 hours the hot solution was filtered. The water-insoluble yellow precipitate weighed 0.04 g.

Ultraviolet spectrum in 0.1 N NaOH solution (see Fig. 1): λ_{max} 390 mμ, lg 3.78; λ_{max} 280 mμ, lg 4.12; λ_{min} 314 mμ, lg 2.76.

Cooling a portion of the filtered solution (50% of the initial volume) gave 0.73 g of precipitate, which was recrystallized from water, and the crystals (0.37 g) separating from a partially cooled solution were filtered, and then converted to the perchlorate. The perchlorate was treated with 0.1 N caustic solution to give pure monoacetate (III), whose solubility in boiling water was 1 : 85.

The fluorescent filtrate from the removal of 0.73 g of crude monoacetate (III) was evaporated to dryness in vacuo (2 hours), and the distillate was titrated with 0.1 N NaOH solution (see table, sample 4). The dry residue weighed 0.4 g, and its solubility in water was 1 : 35.

b) A solution of 1.500 g of pure diacetate (I), dried at 130-135°, in 150 ml of water was boiled with simultaneous steam distillation of the acetic acid formed. Each distillate portion, having a volume of 1000 ml (a total of 21 portions), was titrated with 0.1 N NaOH solution in the presence of phenolphthalein (see Fig. 2). The reaction was terminated after 56 hours, since the distillate no longer contained acetic acid.

Amount of 0.1 NNaOH solution required to titrate the total distillate was 66.50 ml, which represents 100.21%. Theory for one acetyl group is 66.37 ml.

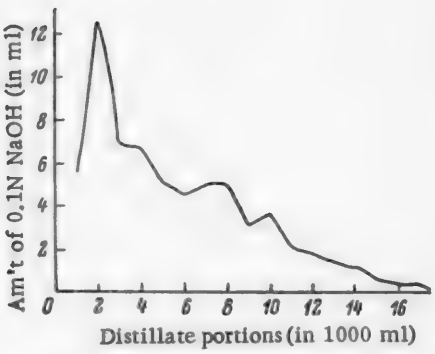


Fig. 2. Titration of the acetic acid distilled off in the hydrolysis of 4,5-bis(acetamido)uracil (I) with water.

The solution was concentrated to a volume of 50 ml, cooled, the precipitate filtered, and it, as well as the filtrate, divided into two equal parts. Half of the precipitate weighed 0.54 g; it was recrystallized twice from water (1 : 85), and then dried in a vacuum-desiccator.

Found %: N 30.32. $C_6H_8O_3N_4$. Calculated %: N 30.43.

The 2nd half of the precipitate was combined with half of the filtrate and the whole heated in the same apparatus with 20 ml of 22% H_2SO_4, with simultaneous steam distillation of the acetic acid formed.

Titration of the distillate required 32.75 ml of 0.1 N NaOH solution, which represents 98.7% of theory. Calculated for one acetyl group is 33.18 ml of 0.1 N NaOH solution.

Reaction of 4-amino-5-acetamidouracil (III) with water. A solution of 0.7587 g of analytical pure (III) 70 ml of water was heated under reflux for 8 hours. Unchanged (III) was recovered quantitatively from the reaction. The same result was obtained when (III) was boiled with water in the presence of steam with partial removal of the water by distillation.

A solution of 0.5440 g of the same (III) in 55 ml of 0.035% acetic acid solution was refluxed for 52 hours.

The solution was cooled and a 10 ml aliquot decanted from the crystalline precipitate. The consumption of alkali was 0.2 ml, which corresponds to the disappearance of 64.2% of the acetic acid taken for reaction and the liberation of ammonia from 3.3% of taken (III).

The remaining 45 ml of yellow-green fluorescent reaction mass was steam-distilled and the distillate titrated for acetic acid, which require 0.89 ml of 0.1 N NaOH solution. Cooling of the residue in the distilling flask gave 0.4 g of (III), while evaporation of the filtrate to dryness gave another 0.13 g of impure material, which was a mixture of (III) and a finely crystalline yellow-green powder.

SUMMARY

It was established that the boiling of 4,5-bis(acetamido)uracil with water results in hydrolytic cleavage with the formation of 4-amino-5-acetamidouracil and acetic acid.

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SYNTHESIS OF 6-ARYLNICOTINIC ACIDS FROM 6-ARYLPYRIDINES

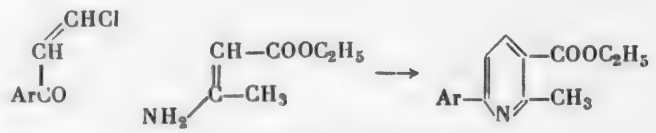
N. K. Kochetkov, E. D. Khomutova, and L. M. Likhosherstov

Moscow State University

Previous investigations in our laboratory showed that β-chlorovinyl ketones and their closest derivatives are convenient starting materials for the synthesis of various compounds of the pyridine series, namely, dialkylnicotinic acids [1], ketones of the pyridine series [2] and substituted α-pyridones [3, 4] and in all these cases alkyl β-chlorovinyl ketones were used.

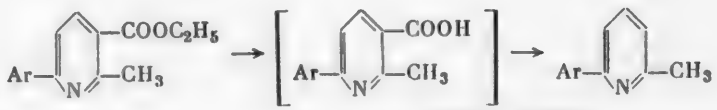
Since aryl β-chlorovinyl ketones have also become generally accessible at the present time [5, 6], it seemed interesting to extend the previously developed method of synthesizing substituted nicotinic acids and dialkylpyridines [1] to the preparation of pyridine derivatives containing aromatic radicals; this is described in our present short note.

The given synthesis may be carried out by condensing aryl β-chlorovinyl ketones with a mixture of acetoacetic ester and ammonia or with isolation of the aminocrotonic ester in an individual state [1]. We chose the second, more convenient variant of the synthesis and carried out the reaction in boiling benzene for 8-14 hours. A double quantity of amino crotonic ester was taken to bind the hydrogen chloride liberated. In all cases, both with phenyl β-chlorovinyl ketone and with its nuclear substituted analogs (o-chloro-, p-chloro- and p-nitrophenyl β-chlorovinyl ketones), the reaction proceeded smoothly and led to 50-65% yields of esters of the corresponding 2-methyl-6-arylnicotinic acids.



Ar = C_6H_5, o-ClC_6H_4, p-ClC_6H_4, p-$NO_2C_6H_4$.

The previously almost unknown 6-arylnicotinic esters obtained could then be used for the synthesis of various pyridine derivatives. We used them for the synthesis of 2-methyl-6-arylpyridines we required and two representatives of which we obtained by dry distillation of sodium salts of arylnicotinic acids in a mixture with soda lime; for this purpose, the appropriate esters were hydrolyzed with alcoholic alkali and the acid obtained was pyrolyzed without purification.



Ar = C_6H_5, p-ClC_6H_4.

Thus, the previously developed method of synthesizing substituted nicotinic acids and disubstituted pyridines is also quite suitable for aromatic derivatives.

EXPERIMENTAL

Ethyl ester of 2-methyl-6-phenylnicotinic acid. Into a flask, fitted with a stirrer and a reflux condenser, were placed 10 g of phenyl β-chlorovinyl ketone and 15.5 g of β-aminocrotonic ester in 60 ml of benzene. The reaction mixture was boiled with stirring for 8 hours, the precipitate removed by filtration and washed with benzene, the solvent distilled from the combined filtrates and the residue vacuum distilled, when a fraction with b. p. 135-170° (1 mm) was collected. A second distillation yielded 7.3 g (51%) of a substance with b. p. 154-160° (1 mm), which crystallized completely. After recrystallization from aqueous alcohol, the substance formed colorless needles with m. p. 45.5-46.5°.

Literature data [7]: B. p. 160-161° (2 mm), m. p. 46-46.5°.

Found %: C 74.61, 74.77; H 6.33, 6.49. $C_{15}H_{15}O_2N$. Calculated %: C 75.60; H 6.22

Ethyl ester of 2-methyl-6-(p-chlorophenyl)-nicotinic acid. This substance was prepared similarly from 29 g of p-chlorophenyl β-chlorovinyl ketone and 38 g of β-aminocrotonic ester in 100 ml of benzene; the reaction mixture was boiled for 12 hours; the yield was 25.1 g (63%), the b. p. 160-175° (1 mm) and the colorless needles had m. p. 47-48° (from aqueous alcohol).

Found %: Cl 12.94, 13.13. $C_{15}H_{14}O_2NCl$. Calculated %: Cl 12.86.

Ethyl ester of 2-methyl-6-(o-chlorophenyl)-nicotinic acid. This substance was prepared similarly from 15 g of o-chlorophenyl β-chlorovinyl ketone and 19.5 g of β-aminocrotonic ester in 70 ml of benzene, which were boiled together for 12 hours; the yield was 11.3 g (55%), the b. p. 140-155° (1 mm) and the colorless needles had m. p. 39-40° (from aqueous alcohol).

Found %: Cl 12.86, 12.70. $C_{15}H_{14}O_2NCl$. Calculated %: Cl 12.86.

Ethyl ester of 2-methyl-6-(p-nitrophenyl)-nicotinic acid. Into a flask fitted with a stirrer and a reflux condenser were placed 17.2 g of p-nitrophenyl β-chlorovinyl ketone and 21 g of β-aminonicotinic ester in 150 ml of benzene and the reaction mixture boiled for 14 hours. The precipitate was removed by filtration and washed with a small amount of dioxane. The benzene solution was evaporated in vacuum, the residue left in a refrigerator and the crystals which separated collected by filtration. A further small amount of the substance was precipitated from the dioxane with water. The total yield was 15.5 g (66%). Recrystallization from aqueous alcohol yielded light yellow needles with m. p. 138-139°.

Found %: C 62.90, 62.81; H 4.70, 4.97. $C_{15}H_{14}O_4N_2$. Calculated %: C 62.94; H 4.89.

2-Methyl-6-phenylpyridine. 6.8 g of the ethyl ester of 2-methyl-6-phenylnicotinic acid was heated with a solution of 3.5 g of sodium hydroxide in 40 ml of alcohol. After being heated for 2.5 hours, the reaction mixture was acidified to congo with concentrated hydrochloric acid and evaporated to dryness. The dry residue was powdered carefully, mixed with 8 g of soda lime, placed in a distillation flask and heated to 350° under reduced pressure. A mixture of an oily substance and water distilled. The distillate was saturated with potassium carbonate, the oily layer separated, the aqueous one extracted with ether and the extract combined with the main material and dried over fired potassium carbonate; the ether was removed and the residue vacuum distilled. After a second distillation, the substance had b. p. 156-160° (20 mm), $n^{20}D$ 1.6090; the yield was 2.9 g (61%).

Literature data [8]: b. p. 117-120° (4 mm), $n^{20}D$ 1.6059.

The picrate, which was obtained by the usual method, formed yellow needles with m. p. 134-135°.

Literature data [9]: m. p. 135°.

2-Methyl-6-(p-chlorophenyl)-pyridine was obtained similarly from 15.8 g of the ethyl ester of 2-methyl-6-(p-chlorophenyl)-nicotinic acid; the yield was 2.5 g (21%), the b. p. 142-152° (8 mm) and the colorless needles had m. p. 62.5-63.5° (from aqueous alcohol).

Found %: Cl 17.68. $C_{12}H_{10}NCl$. Calculated %: Cl 17.49.

SUMMARY

1. The interaction of aryl β-chlorovinyl ketone with β-aminocrotonic ester gave esters of 2-methyl-6-arylnicotinic acids (50-65% yields).

2. Dry distillation of a mixture of salts of 2-methyl-6-arylnicotinic acids with soda lime yielded 2-methyl-6-arylpyridine.

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AMINOACYL AND AMINOALKYL DERIVATIVES OF SOME ALIPHATIC-AROMATIC AMINES

N. K. Kochetkov and N. V. Dudykina

Scientific Research Institute of Pharmacology and Chemotherapy, Academy of Medical Sciences, USSR

In previous communications [1-3] we described chloroacyl derivatives of a series of aliphatic-aromatic amines and some of these were found to be effective antispasmolytics. In continuing the search for agents acting on the central nervous system, among the series of aliphatic-aromatic amines we synthesized some dialkylaminoacyl and dialkylaminoalkyl derivatives of this class of type (A) and (B) and their iodoalkylates.

$$\underset{(A)}{RNHCO(CH_2)_nN(C_2H_5)_2}, \quad \underset{(B)}{RNH(CH_2)_nN(C_2H_5)_2}$$

As starting amines we chose benzylamine and β-phenetylamine, whose β-chloropropionyl derivatives were found to be the most effective in their physiological action [1, 2], and also α,β-diphenylethylamine, N-methyl-α,β-diphenylethylamine, α,β-diphenyl-β-hydroxyethylamine and α,β-diphenyl-β-methoxyethylamine.

The synthesis was carried out by the scheme:

$$\underset{(I)}{RNH_2} \xrightarrow{ClCO(CH_2)_nCl} \underset{(II)}{RNHCO(CH_2)_nCl} \xrightarrow{NH(C_2H_5)_2} \underset{(III)}{RNHCO(CH_2)_nN(C_2H_5)_2 \cdot HCl} \xrightarrow{C_2H_5I} \underset{(IV)}{RNHCO(CH_2)_n\overset{+}{N}(C_2H_5)_3\,\overline{I}}$$

$$\underset{(V)}{RNH(CH_2)_nN(C_2H_5)_2 \cdot 2HCl} \xrightarrow{C_2H_5I} \underset{(VI)}{RNH(CH_2)_n\overset{+}{N}(C_2H_5)_3\,\overline{I}}$$

(Cl(CH₂)ₙN(C₂H₅)₂ and LiAlH₄ are the reagents connecting (II) and (V).)

a) $R = C_6H_5CH_2$, b) $R = C_6H_5CH_2CH_2$, c) $R = C_6H_5CH_2CHC_6H_5$

d) $R = C_6H_5\underset{\displaystyle OH}{\underset{|}{C}}HCHC_6H_5$, e) $R = C_6H_5\underset{\displaystyle OCH_3}{\underset{|}{C}}HCHC_6H_5$.

The derivatives of N-methyl-α, β-diphenylethylamine were obtained by an analogous scheme.

For preparing the N-chloroacyl derivatives (II), we used the previously developed method of acylation by the action of the acid chloride of the halo-substituted acid on the amine in a water-ethyl acetate (or benzene) emulsion in the presence of an equivalent amount of alkali. When used for the first time for α,β-diphenylethylamine) it also gave good results (70-90% yields). When it was more convenient to use the starting amine in the form of the hydrochloride, 2 equivalents of alkali was used for the acylation. The preparation of new representatives of chloroacylamides (IIc, IId and IIe) could be of independent interest, since effective antispasmolytics are known to occur in this series [1, 2]. In the acylation of α,β-diphenyl-β-hydroxyethylamine (Id), the reaction proceeded in a well-defined way and since it occurred at pH values of 7.5-8.0,

it could be assumed that the compounds obtained were N-acyl derivatives (IId), as was confirmed by a negative hydroxamic acid reaction and a negative reaction with ninhydrin.

For preparing the diethylaminoacyl derivatives (III), the chloroacylamides (II) were heated in boiling toluene with diethylamine, which was taken in excess ito bind the hydrogen chloride liberated. The bases (III) formed, were converted into the hydrochlorides by the usual method without isolation in an individual state. The yield of the hydrochlorides was 50-60%. From the point of view of investigating physiological activity in the aliphatic-aromatic amine series, the synthesis of iodoalkylates of the amides (III) was of definite interest. The iodoethylates of these compounds (IV) were obtained by heating the bases (III) (liberated from the hydrochlorides and used without further purification) with ethyl iodide in boiling toluene. They usually precipitated as oils, but could be obtained in the crystalline state after appropriate treatment (50-60% yields).

For comparing the physiological activity of aminoacyl derivatives of aliphatic-aromatic amines with the corresponding aminoalkyl compounds (V), we prepared some representatives of the latter class of compound. Compounds containing the diethylaminoethyl radical (V, n = 2) were by a known method for substances of this type [4], i. e., condensation of the corresponding amines (Ic, d and e) and N-methyl-α,β-diphenylethylamine with the hydrochloride of diethylaminoethylchloride in an aqueous alcohol solution in the presence of bicarbonate. After the usual treatment, the bases of the ethylenediamine derivatives obtained (V) were converted into hydrochlorides without isolation and the yields of the latter were 60-80%. Alkylation of the amino alcohol (Vd) by this method yielded only one substance and since the alkylation of an amino group proceeds considerably more readily than that of a hydroxyl group, the compound obtained was the N-derivative.

For the preparation of diethylaminopropyl derivatives (V, n = 3), for the first time we used the reduction of the acid chlorides of the appropriate diethylaminopropionamides (III, n = 2) with excess lithium aluminum hydride. Due to its simplicity and the high yields (60-80%), this method was very convenient. In all probability, this method will be quite useful for the synthesis of dialkylaminoalkyl derivatives of amines with longer chains (n > 3), whose synthesis is known to involve a series of difficulties.

All the dialkylaminoalkyl derivatives obtained were converted into their iodoethylates (VI) (40-60% yield), when, despite the use of excess ethyl iodide, only quaternary monosalts were obtained. This phenomenon, which is known for other substances of this type [4], is inexplicable at present and requires more detailed investigation. The iodoethylates were obtained as sirups and could only be converted into the crystalline state after appropriate treatment.

The compounds synthesized were tested in the pharmacological department by N. V. Kaverina. All the β-chloropropionamides (II) lacked antispasmolytic action and some of them even increased the movement. The β-dialkylaminoalkylamides (III) did not show analogesic properties and also had an opposite effect in some cases and raised the pain sensitivity threshold. Their quaternary salts (IV) had some hypotensive, spasmolytic and ganglion blocking action.

EXPERIMENTAL

The starting amines were obtained by known methods: α,β-diphenylethylamine was obtained in 61% yield by hydrogenation of desoxybenzoin oxime over nickel and had b. p. 140-142° (5 mm) and $n^{20}D$ 1.5810 [5]; N-methyl-α,β-diphenylethylamine [6] was obtained in 71% yield and had b. p. 135-137° (5 mm), $n^{20}D$ 1.5650; α,β-diphenyl-β-hydroxyethylamine [7] was obtained in 40% yield and had m. p. 122-123°. α,β-Diphenyl-β-methoxyethylamine [8] was obtained, not by the unsatisfactory, known method [9], but by reducing the methyl ether of benzoin oxime over Raney nickel in anhydrous alcohol at room temperature, when the amine was isolated in 70-73% yield as the hydrochloride with m. p. 230-232°.

N-Substituted chloropropionamides (II). We described the synthesis of N-benzyl- and N-phenyl-β-chloropropionamides previously [1, 2]. The other compounds were prepared by the general procedure in [3]. With stirring and cooling to 0. to -5°, 0.025 mole of β-chloropropionyl chloride was added to an emulsion of 0.025 mole of NaOH in 20 ml of water. When the acid chloride had been added, the pH of the mixture was adjusted to 7.5-8.0 and stirring continued for a further 30-40 minutes at room temperature. The ethyl acetate (or benzene) layer was separated, washed with water until neutral, dried over sodium sulfate and the solvent removed in vacuum; the crystalline residue was purified by recrystallization. The data obtained are presented in Table 1.

N-Substituted diethylaminopropionamides (III). A mixture of 0.01 mole of β-chloropropionamide (II) and 0.03 mole of diethylamine in 130 ml of dry toluene was boiled for 2-3 hours with stirring. After removal of the diethylamine hydrochloride, the toluene solution, protected with a trap with alkali, was concentrated in vacuum until no further toluene or diethylamine distilled. The residue was dissolved in 10% hydrochloric acid solution. To remove the neutral substances, the acid solution was extracted 2-3 times with a mixture of benzene and ether (1 : 1), at first at pH 2.0 -3.0 and then at pH 6.5-7.0. To the acid solution was added excess alkali, the liberated base extracted with ether, the extract dried over sodium hydroxide, and excess of a solution of hydrogen chloride in dry ether added. As a rule, the slightly hygroscopic hydrochloride was isolated in the crystalline form. Recrystallization from acetone with the addition of ether yielded a nonhygroscopic, crystalline substance. The results obtained are presented in Table 2.

Iodoethylates of N-substituted diethylaminopropionamides (IV). An aqueous solution of 0.01 mole of the hydrochloride of the N-substituted diethylaminopropionamide was treated with excess alkali, the liberated base carefully extracted with ether, the extract dried, the ether evaporated, 10 ml of dry toluene and 0.07 mole of ethyl iodide added to the base obtained and the mixture boiled in a flask with a reflux condenser for 1.5-2 hours. The iodoethylate, which separated as a heavy yellow oil, was dissolved in acetone and the crystalline substance isolated by the addition of dry ether to the clear acetone solution obtained. The results obtained are presented in Table 2.

TABLE 1

Synthesis of N-Substituted β-Chloropropionamides (II)

Compound	Yield (in %)	M.p. (recrystallization solvent)	% N		% Cl	
			found	calc.	found	calc.
(II c. $n = 2$)	73	132—133° (methanol)	4.68, 4.72	5.11	12.60, 12.69	12.95
(II d. $n = 2$)	83	123—125 (ethyl acetate)	4.74, 4.69	4.61	11.35, 11.52	11.67
(II e. $n = 2$)	94	153—154 (alcohol)	4.72, 4.61	4.38	11.41, 11.21	11.16
N-Methyl derivative (IIc, n = 2)	80	76—77 (alcohol)	4.76, 4.60	4.64	11.58, 11.61	11.75

N-Substituted N',N'-diethylethylenediamines (V, n = 2). To a mixture of 0.05 mole of amine (I) and 6 g of sodium bicarbonate in 15 ml of alcohol was added a solution of 0.08 mole of the hydrochloride of diethylaminoethyl chloride in 30 ml of water over a period of 1 hour with stirring and heating on a water bath at 60-70°, after which the reaction mixture was heated for another hour. The alcohol was removed in vacuum and to the aqueous residue was added a further 50 ml of water and then 20% hydrochloric acid to an acid reaction. The acid solution was extracted 2-3 times with ether and excess alkali added; the liberated base was extracted with ether, the extracts dried and the hydrochloride precipitated with an ether solution of hydrogen chloride and recrystallized from absolute alcohol with the addition of ether. The results obtained are presented in Table 3.

Iodoethylates (VI). The iodoethylates of N-substituted N', N'-diethylethylenediamines were prepared by the method in [4]. A mixture of 0.004 mole of amine dihydrochloride, 0.008 mole of ethyl iodide and 0.008 mole of sodium carbonate in 6 ml of water was boiled for 1.5 hours in a flask with a reflux condenser. The iodoethylate, liberated as a yellow oily precipitate, was washed twice with cold water, dissolved in isopropyl alcohol and the salt crystallized as colorless, lustrous crystals by the slow addition of dry ether. The results are presented in Table 3.

Dihydrochloride of N-benzyl-N',N'-diethyl-1,3-diaminopropane. A suspension of 4 g of the hydrochloride of N-benzyl-β-diethylaminopropionamide in 50 ml of absolute alcohol was slowly added with stirring and

TABLE 2

Synthesis of N-Substituted Diethylaminopropionamides and Their Iodoethylates

Compound	Yield (in %)	M.p. (recrystallization solvent)	% N		% Cl		M.p. of iodoethylate	Analysis of iodoethylate (in %)			
								N		I	
			found	calc.	found	calc.		found	calc.	found	calc.
(IIIa, $n=1$)	54	Oil	—	—	13.74, 13.77	13.81	138—142°	7.23, 7.25	7.44	33.63, 33.74	33.74
(IIIa, $n=2$)	58	53—56° (acetone-ether)	10.6, 10.52	10.34	13.32, 13.19	13.10	98—101	6.98, 6.94	7.17	32.41, 32.40	32.53
(IIIb, $n=2$)	58	87—89 (acetone-ether)	10.25, 10.12	9.83	12.49, 12.53	12.45	119—122	7.15, 7.13	6.93	31.73, 32.08	31.40
(IIIc, $n=2$)	63	115—118 (alcohol-ether)	7.71, 7.75	7.76	9.79, 9.87	9.83	167—169	5.63, 5.54	5.83	26.83, 27.00	26.43
(IIId, $n=2$)	47	163—166 (alcohol)	7.35, 7.38	7.43	9.42, 9.56	9.44	—	—	—	—	—
(IIIe, $n=2$)	58	146—147 (acetone-ether)	7.18, 7.11	7.16	8.91, 9.01	9.01	138—142	5.27, 5.40	5.48	24.86, 25.0	24.87
N-Methyl derivative (IIIc, $n=2$)	30	113—115 (acetone-ether)	7.39, 7.50	7.47	9.61, 9.62	9.46	43—52	5.88, 5.80	5.64	25.34, 25.23	25.68

TABLE 3

Synthesis of N-Substituted N',N'-Diethylethylenediamines and Their Iodoethylates

Compound	Yield (in %)	M. p.	% N		% Cl		M. p. of iodoethylate	Analysis of iodoethylate (in %)			
								N		I	
			found	calc.	found	calc.		found	calc.	found	calc.
(Va)	60	164—167°	9.76	9.55	23.80, 23.78	24.16	—	—	—	—	—
(Vb)	80	136—138	8.69, 8.70	9.12	22.93, 23.09	23.09	—	—	—	—	—
(Vc)	80	120—122	7.62, 7.54	7.58	18.91, 18.81	19.2	143—146	5.77, 5.73	6.19	28.51, 28.67	28.07
(Vd)	74	186—189	7.16, 6.85	7.27	18.74, 18.92	18.41	138—141	5.54, 5.62	5.96	27.24, 27.16	27.11
(Ve)	61.5	230—231	7.24, 7.23	7.01	17.44, 17.30	17.75	135—137	5.59, 5.62	5.80	—	—
N-Methyl derivative (Vc, $n=2$)	66	188—190	7.50, 7.63	7.30	18.99, 18.99	18.50	129—130	—	—	27.38, 27.41	27.22

gentle heating to a solution of 0.9 g lithium aluminum hydride in 30 ml of absolute ether and the mixture heated with stirring for 2 hours. The complex was decomposed with moist ether (20 ml) and then water (10 ml) and afterwards 10% hydrochloric acid was added to an acid reaction; the ether layer was separated and the aqueous layer was treated with excess alkali and extracted with ether; the extract was dried and the dihydrochloride precipitated with a solution of hydrogen chloride in absolute ether. The very hygroscopic crystalline precipitate was collected by filtration, washed with ether and dried in vacuum. Recrystallization from anhydrous alcohol with the addition of ether yielded 2.6 g (60%) of lustrous white crystals with m. p. 164-167°.

Found%: Cl 23.80, 23.78; N 9.76. $C_{14}N_{26}N_2Cl_2$. Calculated%: Cl 24.16; N 9.55.

Dihydrochloride of N-phenetyl-N',N'-diethyl-1,3-diaminopropane was obtained similarly by the reduction of 5 g of the hydrochloride of N-phenetyl- β-diethylaminopropionamide with 2.36 g of lithium aluminum hydride in ether. The colorless needles had m. p. 136-138° and the yield was 4 g (80%).

Found%: Cl 22.93, 23.09; N 8.69. 8.70. $C_{15}H_{28}N_2Cl_2$. Calculated%: Cl 23.09; N 9.12.

SUMMARY

1. The interaction of N-β-chloropropionyl derivatives of benzylamine, phenetylamine, α,β-diphenylethylamine, N-methyl-α,β-diphenylethylamine, α,β-diphenyl-β-hydroxyethylamine and α,β-diphenyl-β-methoxyethylamine with diethylamine yielded the corresponding N-β-diethylaminopropionyl derivatives aof the amines indicated.

2. Condensation of the amines with diethylaminoethyl chloride yielded the corresponding N,N',N'-substituted ethylenediamines.

3. Reduction of N-benzyl- and N-phenetyl-β-diethylaminopropionamides with lithium aluminum hydride gave the corresponding derivatives of 1,3-diaminopropane.

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SYNTHESIS AND CONVERSIONS OF SOME THIAZOLIDINE DERIVATIVES

II. PREPARATION OF AZORHODANINES

A. P. Grishchuk and S. N. Baranov

Lvov Medical Institute

Rhodanine is distinguished by the high lability of the hydrogen atoms in position 5 and due to this it reacts readily with a series of oxo-compounds [1-3]. Rhodanine derivatives have found practical application in analytical chemistry [4], photography [5] and organic synthesis. The interest in thiazolidine derivatives as possible chemotherapeutics arose in connection with the study of the structure of penicillin, which contains a thiazolidine ring in its molecule. The discovery of the fungicidal [6, 7] and antithyroid properties [8] of some thiazolidines increased this interest and served as a stimulus for various syntheses of derivatives of thiazolidine, especially of rhodanine, directed towards the preparation of physiologically active substances [9]. With this aim, we set out to determine the possibility of coupling such active substances as diazonium salts with rhodanine, since there is no data in the literature on such syntheses. In a previous communication [10] we showed that rhodanine, which has weakly acidic properties, readily couples with diazonium salts in a 3-4% aqueous ammonia solution to form previously unknown substances, which we called azorhodanines. This reaction has a general character and gives azorhodanines in high yields (up to 95-98%).

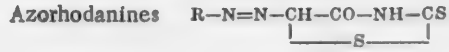
We decided to use the reaction conditions we found for the synthesis of new rhodanine derivatives, from which could be expected biological activity. As is known, the introduction of thiazolidine rings into the molecules of preparations is usually accompanied by a fall in their toxicity [11]. At the same time, the thiazolidine ring contains a grouping which is characteristic of antithyroid substances, namely $>-\underset{\underset{Y}{\|}}{C}-X-$, where X = S, O or NH and Y = S or NH [9]. It should also be noted that azorhodanines in the hydrazone form have a definite structural similarity to certain preparations with an antitubercular activity; the latter are characterized by the grouping $>C=N-\underset{|}{N}-\underset{|}{C}=$ [12]. In order to obtain preparations which were more likely to have physiological action, we used amino compounds which are employed as drugs, namely, anesthesin, sulfanilamide, ethasole, sulfidine, atoxyl and sulfacyl, and also p-aminobenzoic acid.

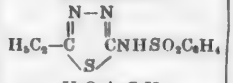
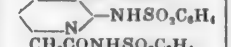
The preparations synthesized were predominantly yellow, finely crystalline powders, which were practically insoluble in water and typical organic solvents such as ether, benzene and chloroform. They were readily soluble in pyridine and, on heating, in the lower alcohols, acetic acid, acetone and dioxane. Being substances of an acid character, the azorhodanines were very readily soluble in alkalis with an intense red color of various shades, which disappeared on acidification. On solution in concentrated sulfuric acid, the compounds gave a red-orange color, which disappeared on dilution with water. Aqueous alcohol solutions of the preparations formed colored precipitates with silver, copper and mercury salts. The given azorhodanines were stable to the action of light, but, as a rule, decomposed on heating. The compounds obtained and their properties are given in the table.

The compounds were purified as follows: (III) – by recrystallization from aqueous alcohol, (IV) – by successive precipitation with water from ethanol, acetone and acetic acid, (V) – by recrystallization from

methanol in the presence of hydrochloric acid, (VI) – by precipitation with acid from 5% NaOH solution with subsequent precipitation with water from ethanol and acetone and (VII) – by 3 precipitations from alcohol.

Azorhodanines

Azorhodanines 

No.	R	Formula	Yield (in %)	M. p.	Nitrogen content (in %)	
					found	calc.
(I)	$HOOCC_6H_4$	$C_{10}H_7O_3N_3S_2$	95	300°(decomp)	14.98	14.94
(II)	$H_5C_2OOCC_6H_4$	$C_{12}H_{11}O_3N_3S_2$	92	228—230 (decomp.)	13.47	13.58
(III)	$H_2NSO_2C_6H_4$	$C_9H_8O_3N_4S_3$	95	268—270 (decomp.)	17.69	17.71
(IV)		$C_{13}H_{12}O_3N_6S_4$	98	153—156	19.36	19.61
(V)	$H_2O_3AsC_6H_4$	$C_9H_8O_4N_3S_2As$	93	210—212 (decomp.)	11.55	11.62
(VI)		$C_{14}H_{11}O_3N_5S_3$	95	174—176	17.19	17.78
(VII)	$CH_3CONHSO_2C_6H_4$	$C_{11}H_{10}O_4N_4S_3$	97	267—269	15.12	15.63

The azorhodanines obtained were investigated for bactericidal activity and were found to be inactive against staphylococci (albus and aureus), dysentery, diptheria, typhoid and tuberculosis bacilli and encapsulated organisms.*

EXPERIMENTAL

5-(4-Carboxyphenylazo)-rhodanine (I). 2.8 g of p-aminobenzoic acid was diazotized and the solution of diazonium salt obtained was added over a period of 15 minutes to a solution of 2.8 g of rhodanine in a mixture of 6 ml of concentrated ammonia and 32 ml of ice-water with vigorous stirring and cooling. To the homogeneous red-orange solution obtained was added 8.0 g of sodium chloride over a period of half an hour and this led to rapid thickening due to crystallization of the dye in the form of the sodium salt; two recrystallizations from a small amount of water gave light orange needles of a crystal hydrate with the composition $C_{10}H_6O_3N_3S_2Na \cdot 2H_2O$, whose color darkened to a bright red on heating.

Direct acidification of an ammonia solution of the dye with hydrochloric acid (1 : 2) precipitated about 5.4 g (95%) of the free acid (I). Recrystallization from 85° alcohol (with the addition of charcoal) gave fine, light yellow needles, which were not heat-sensitive, in contrast to the Na-salt. The dye was practically insoluble in water and ether, but dissolved readily in hot alcohol and dioxane, and less readily so in acetone. It darkened noticeably when heated to 200° and decomposed above 300°.

5-(4-Carbethoxyphenylazo)-rhodanine (II). A diazo solution from 3.3 g of anesthesin was added as described above to a solution of 2.8 g of rhodanine in 6 ml of ammonia and 40 ml of water. After being stirred for 2 hours at 0°, the precipitate was collected, washed with very dilute acid and dried. The yield was 5.7 g (92%). The product was readily soluble in the cold in dioxane, acetone and pyridine and on heating in methanol, ethanol and acetic acid, from which it was readily precipitated with water. Alkaline solutions had a cherry red color; two reprecipitations with water from acetone and then from dioxane with subsequent recrystallization from alcohol gave a light yellow friable powder.

The rest of the azorhodanines were obtained similarly to (I) and (II). The rhodanine was taken in slight excess and sufficient ammonia was used to maintain a slightly ammoniacal medium to the end of the reaction.

* The investigations were carried out in the Microbiology Department of the S. M. Kapustyak Medical Institute, Lvov.

The reaction products were precipitated by careful acidification with dilute hydrochloric acid and after half an hour's standing, they were collected, washed with water and dried in air.

SUMMARY

Coupling diazonium salts of some medicinal amines with rhodanine in an ammoniacal medium yielded new substances, namely azorhodanines, which are 5-substituted rhodanines; these are intensely colored substances, which have acidic properties and give characteristic reactions with silver, copper and mercury salts. The azorhodanines were found to be inactive against the microorganisms investigated.

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SYNTHESIS OF ALKYLCARBONATES OF CELLULOSE AND INVESTIGATION OF THEIR PROPERTIES*

Z. A. Rogovin and Yu. S. Kozlova

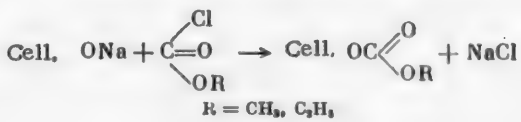
Moscow Textile Institute

Previous investigations in our laboratory [1] showed that the stability of cellulose xanthates was considerably increased by conversion from acid esters to neutral ones. The same rule muxt evidently apply to cellulose carbonates. Preliminary results we obtained in the synthesis of sodium cellulose carbonates showed that this ester of cellulose is very labile and in alkaline solution is hydrolyzed rapidly. Alkylcarbonates of cellulose must be more stable than the corresponding acid esters of cellulose.

As our experiments showed, the alkylcaronates of cellulose are actually much more stable to the action of various reagents than sodium cellulose carbonate and therefore they could be isolated in a pure form and characterized. By comparison of the properties of alkylcarbonates and alkyldithiocarbonates of cellulose, in particular, the stability of these esters towards the action of various reagents, it is possible to determine quite accurately the effect of the character of the acid radical on the properties of esters of cellulose with carbonic and thiocarbonic acids and this is of great interest in the investigation of this class of cellulose esters. The results we obtained in the synthesis of alkylcarbonates of cellulose and their properties are presented briefly in the present article.

EXPERIMENTAL

The alkylcarbonates of cellulose were synthesized by the interaction of chlorocarbonic esters with cellulose in the presence of alkali. This reaction proceeds by the following scheme:



$R = CH_3, C_2H_5$

Methyl and ethyl chlorocarbonates were used for the synthesis of alkylcarbonates of cellulose and gave the methylcarbonate and ethylcarbonate of cellulose, respectively.

An attempt to prepare an alkylcarbonate of cellulose by the direct interaction of methyl chlorocarbonate with cellulose in the presence of anhydrous pyridine did not lead to positive results. No cellulose alkylcarbonate was formed by treatment of cellulose under these conditions for 20-30 hours, both at normal and at elevated temperatures (70-90°). The maximum value of γ for cellulose methylcarbonate, obtained under these conditions, did not exceed 8-9. When the Na-derivative of cellulose was used as the starting material, we were able to obtain a cellulose alkylcarbonate with a considerably higher degree of esterification. The Na-derivative of cellulose was obtained by the method developed in our laboratory [2] by treating "included" cellulose (cotton wool) with sodium isoamylate dissolved in xylene. This method yielded the Na-derivative of cellulose with γ = 230-250.

* 73rd communication in the series "Investigation of the Structure of Cellulose and its Esters".

The Na-derivative of cellulose was treated with methyl chlorocarbonate in sealed ampules at room temperature with periodic shaking. To each gram of cellulose was added 10 ml of methyl chlorocarbonate, which corresponds to about 700% of the amount required theoretically for the preparation of the completely substituted product. After the treatment, the cellulose methylcarbonate obtained was washed with anhydrous methanol and then with acetone until the reaction for chlorine ions disappeared and then dried in a vacuum drying cupboard at 50°. The degree of esterification of the cellulose ester obtained was determined from the methoxyl group content. Such treatment for 60-70 hours yielded cellulose methylcarbonate with $\gamma = 65.72$. A further increase in the treatment time to 140 hours did not lead to an increase in the degree of esterification of the cellulose.

Cellulose methylcarbonate was synthesized by the interaction of alkali cellulose (obtained by treatment of cellulose with 10-45% sodium hydroxide solutions) with methyl chlorocarbonate by the same scheme as when the Na-derivative of cellulose was used. The starting material for the esterification was viscose rayon. The degree of esterification of the methylcarbonate obtained by this method depended to a considerable extent on the concentration of the sodium hydroxide used for mercerization (Table 1).

TABLE 1

Effect of NaOH Concentration Used in Mercerization on the Degree of Esterification of Cellulose Methylcarbonate (Treatment temperature, 20°, treatment time, 24 hours, and 10 ml of esterifying agent per g of cellulose)

NaOH conc. in mercerization (in %)	Composition of alkali cell. (in %)			Amount of OCH_3 groups (in %)	γ of cellulose methylcarbonate
	NaOH	cellulose	H_2O		
10	7	30	60	6.4	38
18	12	30	58	7.7	47
35	23	30	47	11.2	74
45	30	30	40	12.7	87

Cellulose methylcarbonate with $\gamma = 38 - 87$ had the same form as the original cellulose and was insoluble in water, methanol, acetone and benzene.

Cellulose ethylcarbonate was obtained by an analogous scheme by the action of ethyl chlorocarbonate on alkali cellulose (mercerization with 18% sodium hydroxide solution). The starting material used was both "included" cotton and viscose rayon. Cellulose ester with $\gamma = 50 - 65$ was obtained.

The cellulose methyl- and ethylcarbonates we synthesized were examined for their stability towards various treatments in comparison with cellulose methyldithiocarbonate (cellulose methylxanthate). An examination was made of the change in degree of esterification of these cellulose esters after their treatment with dilute solutions of acids and alkalis, and water at 100°, and also the stability of these compounds towards the action of elevated temperatures. After each of these treatments, the cellulose esters were washed with water until neutral, and then with acetone and dried to constant weight at 95-100°. The change in degree of esterification after each of these treatments was determined from the change in the alkoxyl group content.

The results obtained show that the cellulose alkylcarbonates were quite stable to the action of boiling water. Thus, for example, the degree of esterification did not change when they were boiled in water for 6 hours. Cellulose methyldithiocarbonate was less stable to the action of boiling water than cellulose alkylcarbonates. Under the same treatment conditions, 35.2% of the total number of ester groups was eliminated. Cellulose alkylcarbonates were also more stable than cellulose methyldithiocarbonate to the action of 1 N sulfuric acid solution both at 20° and at 100°. Thus, for example, the degree of esterification of cellulose alkylcarbonates did not change during treatment with 1 N sulfuric acid solution at 20° for 24 and 240 hours and at 100° for 0.25-8 hours. When cellulose methyldithiocarbonate was treated with 1 N sulfuric acid solution at 100° for 1 hour, 80.2% of the total number of ester groups was eliminated.

Cellulose alkylcarbonates were also more stable than cellulose methyldithiocarbonate to the action of

elevated temperatures. Thus, when cellulose alkylcarbonates were kept at 100° for 3-12 hours, at 120° for 4 hours and at 140° for 4 and 8 hours in air, their degree of esterification did not change. When cellulose methyldithiocarbonate was kept at 110° for 6 and 12 hours under the same conditions, 13.7 and 32.1% of the total number of ester groups, respectively, were eliminated.

However, cellulose alkylcarbonates were much less stable than cellulose methyldithiocarbonate towards the action of a 1 N solution of sodium hydroxide.

The comparative stability of cellulose alkylcarbonates and methyldithiocarbonate towards the action of 1 N sodium hydroxide solution at 20 and 100° is shown in Table 2.

TABLE 2

Comparative Stability of Cellulose Alkylcarbonates and Alkyldithiocarbonates towards the Action of 1 N NaOH Solution at 20 and 100°

Temp.	Treatment time (in min)	Methylcarbonate			Ethylcarbonate			Methyldithiocarbonate (% of groups hydrolyzed)
		OCH_3 groups (in %)	γ	groups hydrolyzed (in %)	OC_2H_5 groups (in %)	γ	OCH_3 groups (in %)	
20°	—	9.2	58	—	14.1	65	—	—
	5	3.0	17	70	—	—	—	—
	15	0	0	100	—	—	—	—
	60	0	0	100	2.7	10	85	—
	120	—	—	—	0.7	2.5	97	—
	180	—	—	—	0	0	100	—
100	5	0	0	100	0	0	100	18.1
	15	—	—	—	—	—	—	80
	30	—	—	—	—	—	—	100
	60	—	—	—	—	—	—	

Consequently, on the basis of the data obtained, we arrive at the quite definite conclusion that the character of the acid radical in esters of cellulose with carbonic and thiocarbonic acids has a substantial effect on the stability of the cellulose ester towards various treatments. Thus, for example, replacement of a methyldithiocarbonic acid residue in cellulose esters by a methylcarbonic acid residue considerably increases the stability of neutral esters of cellulose towards the action of elevated temperatures, boiling water and especially towards the action of dilute solutions of mineral acids, both at normal and at elevated temperatures. However, this does not occur in regard to the action of alkali. As the data in Table 2 show, cellulose methylcarbonate is much less stable towards the action of dilute alkali solutions than cellulose methylxanthate. Consequently, replacement of a dithiocarbonic acid residue by a carbonic acid residue in a cellulose ester considerably lowers its stability towards the action of dilute alkalis.

The character of the alkyl in cellulose alkylcarbonates also has some effect on the stability of these esters. Thus, for example, under the same treatment conditions, cellulose ethylcarbonates are hydrolyzed more slowly than cellulose methylcarbonates. Like cellulose alkyldithiocarbonates, cellulose alkylcarbonates were insoluble in all the solvents we examined, which makes it impossible to use this new class of cellulose esters for the formation of fibers or films from them.

SUMMARY

1. A method was developed for synthesizing cellulose alkylcarbonates by the interaction of the sodium derivative of cellulose or alkali cellulose with chlorocarbonic esters. Cellulose methylcarbonate with γ = 36 – 87 and cellulose ethylcarbonate with γ = 50 – 68 were obtained.

2. A comparative investigation was made of the stability of cellulose methyl- and ethylcarbonates towards the action of various hydrolyzing agents and also towards the action of elevated temperatures in air.

It was shown that the character of the acid radical in cellulose esters (carbonic or thiocarbonic acid) has a substantial effect on the stability of these cellulose esters towards various treatments. The character of the alkyl in the molecule of cellulose alkylcarbonate also has an effect on the stability of the cellulose ester.

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ORGANOPHOSPHORUS INSECTICIDES

β-FLUOROETHYL ESTERS OF ACIDS OF PHOSPHORUS

M. I. Kabachnik, E. I. Golubeva, D. M. Paikin, M. P. Shabanova,

N. M. Gamper, and L. F. Efimova

Institute of Organoelement Compounds, Academy of Sciences, USSR

Among the many esters of phosphorus acids with insecticidal properties, a particularly outstanding group are derivatives of phosphoric and especially thio- and dithiophosphoric acids, containing in the alcohol radical a hetero atom in a position β to the ester oxygen. To this class of compound belong "Mercaptophos" ("Systox"), which is O,O-diethyl β-ethylmercaptoethyl thiophosphate (a mixture of thione and thiol isomers) [1], "Methylsystox", which is O,O-dimethyl β-ethylmercaptoethyl thiophosphate (also a mixture of isomers), the preparation "M-74", namely O,O-diethyl β-ethylmercaptoethyl dithiophosphate [2], its lower homologs, preparations "M-81" and "M-82" [3], etc. Esters of thio- and dithiophosphoric acids containing chlorine in the β-position of the alkoxyl group are also highly toxic to insects [4, 5]. As far as we know, the corresponding fluorine derivatives have not been studied. In the present article, we describe the synthesis and investigation of the insecticidal properties of the esters of some phosphorus acids, containing fluorine atoms in the β-position of the alkyl group.

A few β-fluoroalkyl esters of phosphorus acids are described in the literature. Thus, Knunyants, Kil'disheva and Bykhovskaya synthesized β,β',β"-trifluorotriethyl phosphite, β,β',β"-trifluorotriethyl phosphate and β-fluoroethyl dichlorophosphate [6]. English investigators prepared β,β'-difluorodiethyl phosphite [7] and β-fluoroethyl diethyl phosphate [8].

Of the esters of phosphorous acid, in addition to the two known phosphites already mentioned, we prepared β-fluorotriethyl phosphite (E-11) and β,β'-difluorotriethyl phosphite (E-20). Both the substance were obtained by the reaction of the appropriate chlorophosphites with β-fluoroethanol in the presence of dimethylaniline. Similarly, we obtained β-fluorotriethyl phosphate (E-32) from diethyl chlorophosphate and β-fluoroethanol in the presence of triethylamine.

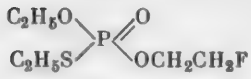
$(C_2H_5O)_2POCH_2CH_2F$ (E-11) $C_2H_5OP(OCH_2CH_2F)_2$ (E-20)

$(FCH_2CH_2O)_2P(S)OH$ (E-30) $(C_2H_5O)_2P(O)OCH_2CH_2F$ (E-32)

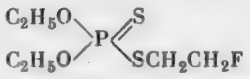
We were most interested in esters of thiophosphoric or dithiophosphoric acids, similar in structure to known insecticides. We introduced the β-fluoroethyl group, either instead of alkyl groups, then the ester molecule had to contain an acyl residue characteristic of substances with insecticidal properties, or the β-fluoroethyl group itself (especially in a β-fluoroethylmercapto group) was considered as an acyl; in this case, the residual valences of the phosphorus had to be attached to alkoxy groups. The addition of sulfur to the β-fluoroethyl phosphites mentioned yielded β-fluorotriethyl thionephosphate (E-3) and β,β'-difluorotriethyl thionephosphate (E-12).

$(C_2H_5O)_2P(S)OCH_2CH_2F$ (E-3)

$C_2H_5OPS(OCH_2CH_2F)_2$ (E-12)



(E-18)



(E-33)

Under normal conditions, β-difluorodiethyl phosphite does not add sulfur. However, as we found previously in the case of dialkyl phosphites [9], in a dioxane medium sulfur added normally with the formation of β,β'-difluorodiethyl thiophosphate (E-30).

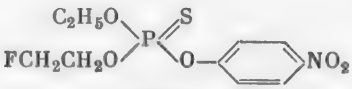
A Pishchimuka rearrangement [10] by heating β-fluorotriethyl thionephosphate with ethyl bromide yielded, O,S-diethyl O-β-fluoroethyl thiophosphate (E-18). We obtained the isomeric thiol ester (E-31) by alkylation of sodium diethyl thiophosphate with fluorobromoethane. As one of us and Mastryukova [11] showed, the alkylation of sodium dialkylthiophosphates proceeds at the sulfur with transfer of the reaction center.

$$(C_2H_5O)_2PSONa + BrCH_2CH_2F \longrightarrow \underset{\text{(E-31)}}{(C_2H_5O)_2P(O)SCH_2CH_2F} + NaBr$$

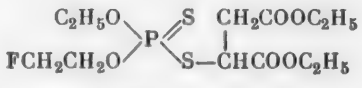
By a similar alkylation of sodium diethyl dithiophosphate with fluorobromoethane, we obtained, O,O-diethyl β-fluoroethyl dithiophosphate (E-33). Then, starting from phosphorus thiotrichloride, we synthesized β-fluoroethyl dichlorothionephosphate (E-49) and β-fluorodiethyl chlorothionephosphate (E-48) by the following scheme:

$$PSCl_3 + FCH_2CH_2OH \longrightarrow \underset{\text{(E-49)}}{FCH_2CH_2OPSCl_2} \xrightarrow[(C_2H_5)_3N]{C_2H_5OH} \underset{\text{(E-48)}}{\begin{matrix} C_2H_5O \\ FCH_2CH_2O \end{matrix}\!\!>\!P(=S)\!-\!Cl}$$

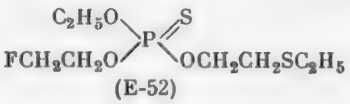
The latter served as an intermediate for the synthesis of a series of fluorine-containing analogs of known insecticides (E-50, E-51 and E-52).



(E-50)



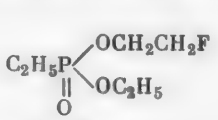
(E-51)



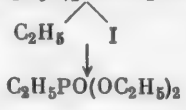
(E-52)

We prepared β-fluoroethyl esters of alkylphosphinic acids by two methods. In the first one, fluorine-containing trialkyl phosphites were subjected to an Arbuzov rearrangement [12]. The action of ethyl iodide on β-fluorotriethyl phosphite simultaneously gave two products, namely, β-fluorodiethyl ethylphosphinate (E-9) and diethyl ethylphosphinate, which did not contain fluorine. The formation of the two substances was the result of cleavage of ethyl iodide, in the first case, and fluoriodoethane, in the second, from the intermediate phosphonium complex.

$$(C_2H_5O)_2POCH_2CH_2F + C_2H_5I \longrightarrow (C_2H_5O)_2POCH_2CH_2F$$

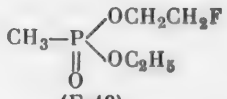


(E-9)



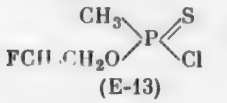
The reaction of β-fluorotriethyl phosphite with methyl iodide formed a single reaction product, namely β-fluorodiethyl methylphosphinate (E-19).

In the second method, we reacted β-fluoroethanol with acid chlorides of alkylphosphinic acids in the presence of triethylamine. This gave, for example, β,β'-difluorodiethyl methylphosphinate (E-28).



(E-19)

$CH_3PO(OCH_2CH_2F)_2$
(E-28)

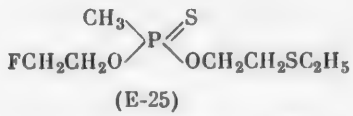


(E-13)

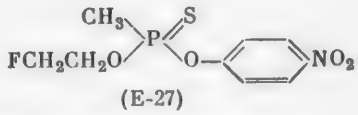
$CH_3PS(OCH_2CH_2F)_2$
(E-29)

As the main intermediate for the preparation of β-fluorinated derivatives of methylthiophosphinic and methyldithiophosphinic acids we used the acid chloride of methylthiophosphinic acid, which is readily obtained by the method described by one of us and N. N. Godovikov [13]. Thus, by the action of β-fluoroethanol on it in the presence of triethylamine, depending on the ratio of the reagents, we obtained β-fluoroethyl methylchlorothionephosphinate (E-13) or β,β'-difluorodiethyl methylthionephosphinate (E-29).

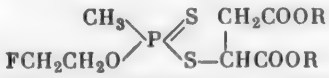
In the presence of triethylamine, ethylmercaptoethanol and p-nitrophenol reacted with β-fluoroethyl chlorothionemethylphosphinate (E-13) with fthe formation of the corresponding mixed esters (E-25) and (E-27). The reaction of β-fluoroethyl methylchlorothionephosphinate with esters of mercaptosuccinic acid yielded O-β-fluoroethyl, α,β-dicarbalkoxyethyl dithiomethylphosphinates (E-14, E-15 and E-16).



(E-25)

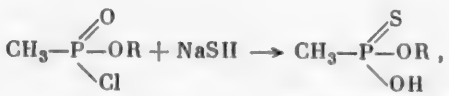


(E-27)



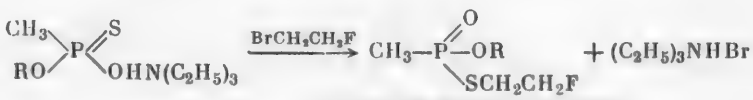
R = CH_3 (E-15); R = C_2H_5 (E-14); R = изо-C_3H_7 (E-16).

We synthesized esters containing a β-fluoroethylmercapto group by the following method. First, the action of sodium hydrosulfide on alkyl esters of methylchlorophosphinic acid yielded acid esters of methylthiophosphinic acids:



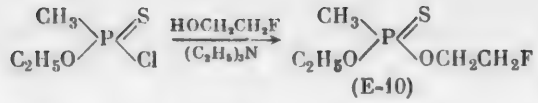
R = CH_3 (E-37); R = C_2H_5 [14].

and then the triethylammonium salts of these acid esters were alkylated with bromofluoroethane.



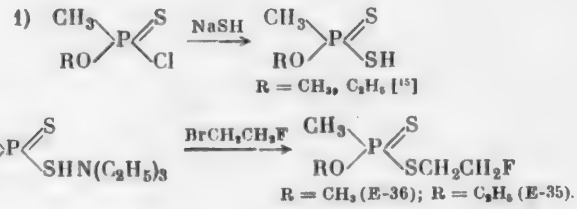
R = CH_3 (E-39); R = C_2H_5 (E-38)

We obtained the corresponding thione isomer by the reaction of ethyl chlorothionemethylphosphinate with β-fluoroethanol in the presence of triethylamine.



(E-10)

Finally, starting from the alkyl esters of methylchlorothionephosphinic acid, we obtained the corresponding dithio derivatives.



The β-fluoroethyl esters of phosphorus acids synthesized were tested under laboratory conditions as contact and systemic insecticides. They were used in the form of emulsions prepared from concentrates containing 30% of the active principle and 70% of the auxiliary substance OP-7. Experiments on the contact action

Activity of β-Fluoroethyl Esters of Phosphorus Acids as Contact and Systemic Insecticides

Substance No.	LD 95-100 for muchnistyi chervets [flour scale insects] (%)	Mortality of grasshopper larvae (in %)	Substance No.	LD 95-100 for muchnistyi chervets [flour scale insects] (%)	Mortality of grasshopper larvae (in %)
E-31	0.025	33.3	E-52	0.15	—
E-18	0.1	5.0	E-9	0.2	0
E-33	0.2	86.7	E-19	0.4	3.3
E-3	0.3	—	E-28	0.3	18.3
E-32	0.5	21.3	E-29	>0.5	3.3
E-12	0.2	6.7	E-25	0.2	0
E-39	<0.1	38.3	E-27	0.15	0
E-38	0.1	3.3	E-14	0.2	3.3
E-35	0.15	—	E-15	0.2	0
E-36	0.15	98.3	E-16	0.2	0
E-50	0.2	18.3	Thiophos	>0.025	—
E-51	0.15	—	Mercaptophos (mixture of isomers)	0.015	96.7

were carried out on larvae of older muchnistyi chervets (Pseudococcus maritimus Ehr.) by spraying the insects. Systemic action was studied on larvae of the 2nd stage of the Italian grasshopper (Calliptamus italicus L.) by treating seed before sowing. The seed of spring wheat was sprayed with 0.6% (on the active principle) of emulsions of the compounds, dried in air and sown in pots after 1 day. The grasshopper larvae were put onto the three-day old wheat shoots and kept on them for 7 days. The action of the compounds on the insects was determined on the 1st, 3rd, 5th and 7th days. The results of the experiments on contact action determined the concentration of emulsion producing 95-100% dead or paralyzed individuals of muchnistyi chervets (LD 95-100) and those on systemic action gave the percent mortality of the grasshopper larvae. Data from experiments on 7th day counts are given in the Table. As the data in the Table show, the β-fluoroethyl esters of phosphorus acids tested on the whole have weak insecticide properties, with the exception of compounds (E-31), (E-33) and (E-36). Of these, in contact action on muchnistyi chervets, substance E-31 (O,O-diethyl S-β-fluoroethyl thiolphosphate) was found to be equivalent to Thiophos, while E-33 (O,O-diethyl S-β-fluoroethyl dithiosphos-

phate) and E-36 (O-methyl S-β-fluoroethyl dithiomethylphosphinate) were active systemically against grasshopper larvae. On feeding grasshopper larvae with wheat shoots grown from seed treated with 0.6% emulsions of compounds E-33 and E-36, 86.7 and 98.3% mortality of the insects, respectively, was achieved against 96.7% in the case of Mercaptophos. All the other compounds were more or less inferior to Thiophos and Mercaptophos.

Analysis of the data on the activity of the compounds in separate groups gives the following picture. Of the derivatives of diethylphosphoric acid and thione-, thiol- and dithiophosphoric acid (E-31, E-18, E-33, E-3, and E-32), the most toxic against muchnistyi chervets by contact action was the derivative of thiophosphoric acid E-31, the next place was occupied by the derivative of thiolphosphoric acid E-18 and after that, the derivative of dithiophosphoric acid E-33. The least toxic were derivatives of thionephosphoric acid E-3 and especially of phosphoric acid E-32. Of the two compounds of thionephosphoric acid (E-3 and E-12), substance E-12, containing two β-fluoroethyl radicals, was somewhat better than the compound E-3 with one β-fluoroethyl radical. For grasshopper larvae, fed on wheat plants rendered toxic with these compounds, the highest activity was shown by derivative of dithiophosphoric acid E-33, while the derivatives of phosphoric (E-32) and thiolphosphoric acids (E-31) were quite weak insecticides and the derivative of thiophosphoric acid E-18 can be considered inactive. Of the esters of methylphosphinic and thiol- and dithiomethylphosphinic acids, containing the β-fluoroethylmercapto group (E-38, E-39, E-35, E-36 and E-19), in contact action against muchnistyi chervets, the derivatives of methylthiophosphinic acid (E-38 and E-39) were slightly more toxic than the derivatives of methyldithiophosphinic acid (E-35 and E-36), while the latter were more toxic than the derivative of methyldiothiophosphinic acid (E-35 and E-36), while the latter were more toxic than the derivative of methylphosphinic acid (E-19). As regards systemic action, here in activity against grasshopper larvae, the derivative of dithiophosphinic acid E-36 stands out and gives results similar to those of Mercaptophos. Fluorine-containing analogs of Thiophos (E-50), Malathione (E-51) and Systox (E-52) were weaker insecticides than the same compounds without fluorine. The β-fluoroethyl esters of alkylphosphinic acids (E-9 and E-19) did not show systemic action and had low activity in contact application. In the latter case, the ethyl compound (E-9) was more toxic than the methyl (E-19). Among the derivatives of O,β-fluoroethyl S-α,β-dicarbalkoxyethyl methyldithiophosphinic acid (E-14, E-15 and E-16), which were characterized by weak insecticide properties, no differences were observed depending on this or that alkoxy group. Thus, according to the data of our investigations, the bulk of the esters of some phosphorus acids synthesized, containing a fluorine atom in the β-position of the alkyl group, possessed weak insecticide properties. Only a few of them were equivalent to known insecticides in activity.

EXPERIMENTAL

β-Fluorotriethyl phosphite (E-11). To an ether solution of 10 g of diethyl chlorophosphite and 7.72 g of dimethylaniline was added 4 g of β-fluoroethanol. We isolated 5 g (43%) of the substance.

B. p. 41-42° at 1.5 mm, $n^{20}D$ 1.4208, d^{20}_4 1.0980, MR_D 42.70; calc. 43.02.

Found %: C 39.30, 39.34; H 7.65, 7.70. $C_6H_{14}O_3PF$. Calculated %: C 39.12; H 7.60.

β,β'-Difluorotriethyl phosphite (E-20). 12.8 g of fluoroethanol was added to an ether solution of 14.7 g of ethyl dichlorophosphite and 24.2 g of dimethylaniline. The reaction mixture was cooled. The yield was 36% (7.3 g).

B. p. 47-48°(0.5mm) $n^{20}D$ 1.4200, d^{20}_4 1.1772, MR_D 43.43; calc. 43.06.

Found %: P 15.24, 15.16. $C_6H_{13}O_3PF_2$. Calculated %: P 15.34.

β,β'-Difluorodiethyl phosphite (E-17). From 5.23 g of PCl_3 and 7.3 g of fluoroethanol with cooling, we obtained 5.0 g of di-β-fluoroethyl phosphite.

B. p. 102° at 2 mm, $n^{20}D$ 1.4143, d^{20}_4 1.3738, MR_D 31.67; calc. 31.62.

Found %: P 5.56, 5.44. $C_4H_9O_3PF_2$. Calculated %: P 5.61.

β-Fluorotriethyl phosphate (E-32). To an ether solution of triethylamine (5.1 g) was gradually added a mixture of dichlorophosphate (8.63 g) and fluoroethanol (3.2 g). The reaction was complete after 3 hr heating at the boiling point of ether. We obtained 5.7 g (57%) of the substance.

B. p. 78-79° at 0.5 mm, $n^{20}D$ 1.4051, d^{20}_4 1.1723, MR_D 41.82; calc. 41.95.

Found %: C 36.00, 35.93; H 7.03, 6.97; P. 15.22, 15.15. $C_6H_{14}O_4PF$. Calculated %: C 36.00; H 7.00; P 15.50.

β-Fluorotriethyl thionephosphate (E-3). To 10.2 g of β-fluorotriethyl phosphite was added 1.8 g of sulfur. The reaction preceeded with the evolution of heat. The end of the reaction was determined from the change in color of the reaction mixture. We obtained 4 g (33%) of the substance.

B. p. 65-66° at 0.5 mm, $n^{20}D$ 1.4570, d^{20}_4 1.1876, MR_D 49.53; calc. 49.44.

Found %: C 33.29, 33.03; H 6.39, 6.31; P 14.31, 14.10. $C_6H_{14}O_3PF$. Calculated %: C 33.33; H 6.48; P 14.35.

β,β'-Difluorotriethyl thionephosphate (E-12). 13.5 g of β,β'-difluorotriethyl phosphite were heated with 2.15 g of sulfur for 2.5 hours at 130°. The fraction isolated weighed 3.3 g (23%).

B. p. 86-88° at 3 mm, $n^{20}D$ 1.4580, d^{20}_4 1.2686, MR_D 50.33; calc. 49.78.

Found %: P 12.98, 12.85. $C_6H_{13}O_3PF_2$. Calculated %: P 13.25.

β,β'-Fluorodiethyl thiophosphate (E-30). 17.4 g of β,β'-fluorodiethyl phosphite and 3.2 g of sulfur were heated in dioxane in a flask with a reflux condenser for 16 hours at the boiling point of the dioxane. After removal of the dioxane, the residue was distilled in high vacuum. We obtained 9.3 g (45%) of the substance.

B. p. 97-100° at 0.03 mm, $n^{20}D$ 1.4595, d^{20}_4 1.4238, MR_D 39.61; calc. 40.12.

Found %: P 15.01, 14.98. $C_4H_9O_3PSF_2$. Calculated %: P 15.05.

O,S-Diethyl-O-β-fluoroethyl thiophosphate (E-18). 10.8 g of β-fluorotriethyl thiophosphate were heated in a sealed tube with 43.6 g of ethyl bromide at 140-150° for 5 hours. We obtained 1.6 g (14%).

B. p. 81-82° at 0.5 mm, $n^{20}D$ 1.4596, d^{20}_4 1.2012, MR_D 49.21; calc. 49.04.

Found %: P 14.01, 14.12. $C_6H_{14}O_3PSF$. Calculated %: P 14.35.

O,O-Diethyl S-β-fluoroethyl thiolphosphate (E-31). To an alcohol solution of 6.4 g of sodium diethyl thiophosphate was added 8.5 g of 1,2-fluorobromoethane. The reaction was carried out with stirring for 4 hours at 80-85° (bath temperature). We obtained 3.8 g (51%) of substance.

B. p. 82-83° at 0.5 mm, $n^{20}D$ 1.4530, d^{20}_4 1.1882, MR_D 49.13; calc. 49.05.

Found %: C 33.47, 33.34; H 6.68, 6.62; P 14.41, 14.56; F 9.36, 9.06. $C_6H_{14}O_3PSF$. Calculated %: C 33.33; H 6.48; P 14.26; F 8.79.

O,O-Dithyl-S-β-fluoroethyl dithiophosphate (E-33). To an alcohol solution of 5.6 g of potassium diethyl dithiophosphate was added 4.0 g of fluorobromoethane. The reaction mixture was heated. We obtained 4.3 g (74%) of substance.

B. p. 88° at 1.5 mm, $n^{20}D$ 1.4990, d^{20}_4 1.1973, MR_D 56.89; calc. 56.81.

Found %: C 30.98, 31.19; H 5.93, 6.21; P 13.62, 13.35. $C_6H_{14}O_2PS_2F$. Calculated %: C 31.03; H 6.03; P 13.36.

β-Fluoroethyl dichlorothionephosphate (E-49). This material (114 g; 58%) was obtained by heating phosphorus thiotrichloride (84 g) and fluoroethanol (32 g).

B. p. 67-68° at 8 mm, $n^{20}D$ 1.5041, d^{20}_4 1.5108, MR_D 38.62; calc. 38.14.

Found %: C 12.26, 12.05; H 2.24, 2.14; Cl 36.24, 36.31. $C_2H_4OPSCl_2F$ Calculated %: C 12.19; H 2.05; Cl 36.00.

β-Fluorodiethyl chlorothionephosphate (E-48). This product was obtained from 4.6 g of alcohol and 19.7 g of β-fluoroethyl dichlorothionephosphate in the presence of triethylamine (10.1 g) in an ether medium with cooling. The yield was 58.0% (10.8 g).

B. p. 62-63° at 1.5 mm, $n^{20}D$ 1.4712, d^{20}_4 1.3309, MR_D 43.38; calc. 43.79.

Found %: P 14.72, 14.64; Cl 17.72, 1764. $C_4H_9O_2PSClF$. Calculated %: P 14.99; Cl 17.18.

β-Fluorodiethyl 4-nitrophenyl thionephosphate (E-50). With stirring, to an ether solution of 2.02 g of triethylamine was added β-fluoordiethyl chlorothionephosphate (4.15 g) and then p-nitrophenol (2.78 g). The mixture was heated for 5 hours. We obtained 3.6 g (57.8%) of product.

B. p. 134-135° at $1 \cdot 10^{-4}$ mm, $n^{20}D$ 1.5290, d^{20}_4 1.3469.

Found %: C 38.53, 38.37; H 4.57, 4.37. $C_{10}H_{13}O_5PSNF$. Calculated %: C 38.83; H 4.23.

O,O-β-Fluorodiethyl α, β-dicarbethoxyethyl dithiophosphate (E-51). To an ether solution of 3.03 g of triethylamine, a mixture consisting of 6.2 g of β-fluorodiethyl chlorothionephosphate and 6.18 g of diethyl thiosuccinate was added dropwise. The reaction was carred out at room temperature. After removal of the ether, the residue was vacuum distilled. We obtained 4.6 g (47%) of substance.

B. p. 110-115° at about $1 \cdot 10^{-6}$ mm, $n^{20}D$ 1.4840, d^{20}_4 1.2297, MR_D 87.57; calc. 87.64.

Found %: C 38.25, 38.17; H 6.03, 5.93. $C_{12}H_{22}O_6PS_2F$. Calculated %: C 38.35; H 5.90.

β-Fluoro-β'-ethylmercaptotriethyl thionephosphate (E-52). To an ether solution of 4.1 g of triethylamine was added a mixture of 8.2 g of β-fluorodiethyl thionephosphate and 4.24 g of β-hydroxydiethyl sulfide. We obtained 4.4 g (40%) of the substance.

B. p. 72-74° at $1 \cdot 10^{-4}$ mm, $n^{20}D$ 1.4831, d^{20}_4 1.1970, MR_D 65.85; calc. 66.65.

Found %: C 34.22, 34.46; H 6.49, 6.26. $C_8H_{18}O_3PS_2F$. Calculated %: C 34.81; H 6.57.

β-Fluorodiethyl ethylphosphinate (E-9). 12.6 g of β-fluorotriethyl phosphite and 10.6 g of ethyl iodide were heated in a sealed tube for 5 hours at 130°. A decrease in volume was noticed. Two fractions were obtained: and 1st boiling at 90-92° at 19 mm, 4.5 g (40%) and corresponding in its constants ($n^{20}D$ 1.4162, d^{20}_4 1.1380) to diethyl ethylphosphinate; the 2nd with b. p. 70-71° at 2 mm (6 g; 58%) was β-fluorodiethyl ethylphosphinate.

$n^{20}D$ 1.4205, d^{20}_4 1.1380, MR_D 40.92; calc. 40.82

Found %: C 38.95, 38.66; H 7.63, 7.74; P 16.84, 16.86. $C_6H_{14}C_3PF$. Calculated %: C 39.13; H 7.60; P 16.85.

β-Fluorodiethyl methylphosphinate (E-19). 18.4 g of β-fluorotriethyl phosphite and 14.2 g of methyl iodide were heated in a sealed tube for 3.5 hours at 125-130°. A high pressure was found on opening the tube. We obtained 9.2 g (55%) of the substance.

B. p. 61-62° at 0.5 mm, $n^{20}D$ 1.4147, d^{20}_4 1.1777, MR_D 36.12; calc. 36.20.

Found %: P 18.43, 18.08. $C_5H_{12}O_3PF$. Calculated %: P 18.23.

β,β'-Difluorodiethyl methylphosphinate (E-28). An ether solution of a mixture of 12.8 g of fluoroethanol and 13.3 g of the diacid chloride of methylphosphinic acid was added to an ether solution of 20.2 g of triethylamine. We obtained 12 g (64%) of the substance.

B. p. 101° at 1.5 mm, $n^{20}D$ 1.4146, d^{20}_4 1.3027, MR_D 36.28; calc. 36.25.

Found %: C 32.22, 32.33; H 6.34, 6.27; F 20.18, 20.17. $C_5H_{11}O_3PF_2$. Calculated %: C 31.91; H 5.85; F 20.20.

β,β'-Difluorodiethyl methylthionephosphinate (E-29). This substance was obtained from 14.9 g of the diacid chloride of methylthiophosphinic acid and 12.8 g fluoroethanol in the presence of 20.2 g of triethylamine. The reaction was carried out in ether solution. The yield was 4.6 g (23%).

B. p. 64-65° at 0.5 mm, $n^{20}D$ 1.4658, d^{20}_4 1.2776, MR_D 44.12; calc. 43.73.

Found %: C 29.43, 29.35; H 5.41, 5.42; F 18.52, 18.45; S 15.38, 15.33. $C_5H_{11}O_2PSF_2$. Calculated %: C 29.41; H 5.39; F 18.62; S 15.68.

β-Fluoroethyl methylchlorothionephosphinate (E-13). This substance was obtained from 14.9 g of the diacid chloride of methylthiophosphinic acid and 6.4 g of fluoroethanol in the presence of 10.1 g of triethylamine in an ether medium. The yield was 7.2 g (41%).

B. p. 67-68° at 5 mm, $n^{20}D$ 1.4998, d^{20}_4 1.3392, MR_D 38.75; calc. 38.04.

Found %: P 17.96, 17.81. $C_3H_7OPSFCl$. Calculated %: P 17.56.

β-Fluoro-β'-ethylmercaptodiethyl methylthionephosphinate (E-25). This substance was obtained from 10 g of β-fluoroethyl methylchlorothionephosphinate (E-13) and 6.6 g of β-hydroxydiethyl sulfide in an ether medium in the presence of 6.3 g of triethylamine by heating on a water bath. The yield was 7.3 g (57.9%).

B. p. 70-72° at 0.02 mm, $n^{20}D$ 1.5045, d^{20}_4 1.1949, MR_D 61.03. Calc. 60.99.

Found %: C 33.73, 33.53; H 6.56, 6.63; F 7.71, 7.24. $C_7H_{16}O_2PS_2F$. Calculated %: C 34.15; H 6.50; F 7.72.

β-Fluoroethyl p-nitrophenyl methylthionephosphinate (E-27). To an ether solution of 7.26 g of triethylamine was added a mixture of 11.5 g of (E-13) and 10.0 g of p-nitrophenol in ether. The reaction mixture was heated. We obtained 6.7 g (60%) of substance.

B. p. 102-103° at 0.01 mm, $n^{20}D$ 1.5620, d^{20}_4 1.3748, MR_D 65.80; calc. 65.00.

Found %: C 38.58, 38.50; H 3.98, 4.06; F 6.89, 6.91; P 11.03, 10.95. $C_9H_{11}O_4PNSF$. Calculated %: C 38.71; H 3.94; F 6.81; P.11.11.

O-β-Fluoroethyl S-α-β-dicarbalkoxyethyl methyldithiophosphinates (E-14, E-15 and E-16). β-Fluoroethyl methylchlorothionephosphinate, triethylamine and mercaptosuccinic ester were used for the reaction in molar ratios. The experiments were carried out in ether solution with water cooling. After the addition of the mixture, the mass was heated for 2 hours at a bath temperature of 40-45°. After removal of the ether, the residue was distilled in high vacuum.

E-14 (R = C_2H_5). Yield 56%. The product was a viscous liquid with a slight yellow color. B. p. 109-110° at 0.005 mm, $n^{20}D$ 1.9090, d^{20}_4 1.2530, MR_D 82.46; calc. 82.08.

Found %: C 38.25, 38.27; H 5.83, 5.74. $C_{11}H_{20}O_5PS_2F$. Calculated %: C 38.14; H 5.49.

E-15 (R = CH_3). Yield 72%. B. p. 96-97 at 0.008 mm, $n^{20}D$ 1.5163, d^{20}_4 1.3061, MR_D 73.2; calc. 72.84.

Found %: C 34.15, 34.07; H 5.16, 5.30. $C_9H_{15}O_5PS_2F$. Calculated %: C 34.06; H 4.73.

E-16 (R = iso-C_3H_7). Yield 60%. The viscous liquid had b. p. 100-101° at 0.015 mm, $n^{20}D$ 1.5030, d^{20}_4 1.2108, MR_D 91.31; calc. 91.32.

Found %: P 8.14, 8.02. $C_{13}H_{24}O_5PS_2F$. Calculated %: P 8.28.

Monomethyl methylthionephosphinate (E-37). Sodium hydrosulfide was prepared by the action of hydrogen sulfide on sodium alcoholate in excess methanol. The alcohol was then evaporated and replaced by benzene. The methyl ester of methylchlorophosphinic acid (12.85 g) was then added gradually. The reaction was complete after 3 hours heating at the boiling point of benzene. The sodium salts were removed by extraction with water. The acidified reaction mixture was extracted with ether. The ether extracts were dried with sodium sulfate. We obtained 4.8 g (38%) of substance.

B. p. 63-64° at 1 mm, $n^{20}D$ 1.5058, d^{20}_4 1.2439, MR_D 30.09; calc. 29.78.

Found %: C 19.57, 19.62; H 5.80, 5.65; P 24.60, 24.65; S 25.34, 25.56. $C_2H_7O_2PS$. Calculated %: C 19.04; H 5.55; P 24.60; S 25.40.

The corresponding ethyl ester was obtained analogously.

O-Ethyl S-β-fluoroethyl methylthiolphosphinate (E-38). This substance was obtained from 8.5 g of monoethyl methylthionephosphinate and 7.7 g of fluorobromoethane in the presence of 6.2 g of triethylamine. We obtained 4.8 g (44%) of the substance.

B. p. 82° at 1 mm, $n^{20}D$ 1.4725, n^{20}_4 1.1986, MR_D 43.49; calc. 43.29.

Found %: C 32.46, 32.29; H 6.66, 6.53. $C_5H_{12}O_2PSF$. Calculated %: C 32.26; H 6.45.

O-Methyl β-Fluoroethyl methylthiophosphinate (E-39). 5.2 g of fluorobromoethane was added to an ether solution of 5.1 g of monomethyl methylthionephosphinate and 4.2 g of triethylamine. After being heated for 3 hours, the ether solution was separated from the triethylamine hydrobromide and dried over sodium sulfate. We obtained 2.7 g (40%) of product.

B.p. 59 – 60° at 1 mm, n^{20}_D 1.4720, d^{20}_4 1.2401, MR_D 38.86; calc. 38.68.

Found%: C 28.15, 28.24; H 6.17. 6.16. $C_4H_{10}O_2PSF$. Calculated%: C 27.91; H 5.81. P 16.66.

O-β-Fluorodiethyl methylmonothiophosphinate (E-10). To a mixture of 5.28 g of monoethyl methylchlorothiophosphinate, 3.37 g of triethylamine and benzene (25 ml) was added 2.13 g β-fluoroethyl alcohol. The reaction proceeded with slight evolution of heat. We obtained 1.5 g (24%) of substance.

B. p. 43-44° at 0.5 mm, $n^{20}D$ 1.468, d^{20}_4 1.1682, MR_D 44.26; calc. 43.70.

Found %: C 32.14, 32.14; H 6.13, 6.42; P. 16.48, 16.39. $C_5H_{12}O_2PSF$. Calculated %: C 32.25; H 6.44; P 16.66.

O-Ethyl S-β-fluoroethyl methyldithiophosphinate (E-35). To an ether solution of 6.5 g of triethylamine was added a mixture of 9.9 g of monoethyl methyldithiophosphinate and 8.1 g of fluorobromoethane with stirring. We obtained 11.5 g (90%) of the substance.

B. p. 68° at 0.5 mm, $n^{20}D$ 1.5230, d^{20}_4 1.2035, MR_D 51.27; calc. 51.06.

Found %: C 29.89, 29,67; H 5.69, 5.94. $C_5H_{12}OPS_2F$. Calculated %: C 29.70; H 5.94.

O-Methyl S-β-fluoroethyl methyldithiophosphinate (E-36). The salt of monomethyl methyldithiophosphinate was obtained from 7.1 g of this acid and 5.1 g of triethylamine in ether; 6.4 g of fluorobromoethane was added at room temperature and the flask then heated at the boiling point of ether for 3 hours. We obtained 7.7 g (83%) of product.

B. p. 84-85° at 3 mm, $n^{20}D$ 1.5385, d^{20}_4 1.2599, MR_D 46.71; calc. 46.45.

Found %: C 25.25, 25.34; H 5.31, 5.25; F 10.11, 10.17. $C_4H_{10}OPS_2F$. Calculated %: C 25.53; H 5.32; F 10.10.

SUMMARY

1. A series of derivatives of thio- and dithiophosphoric and thio- and dithioalkylphosphinic acids, containing β-fluoroethyl groups, was synthesized.

2. The substances obtained were tested as contact and systemic insecticides. Most of them had weak insecticidal properties and only some of them, namely O,O-diethyl S-β-fluoroethyl thiolphosphate (E-31) and O-methyl S-β-fluoroethyl dithiomethylphosphinate (E-36), were equivalent to Thiophos (the first) and Mercaptophos (the second).

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ORGANOPHOSPHORUS INSECTICIDES

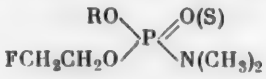
SOME ESTER-AMIDES OF ACIDS OF PHOSPHORUS CONTAINING β-FLUOROETHYL GROUPS

M. I. Kabachnik, E. I. Golubeva, D. M. Paikin, M. P. Shabanova,

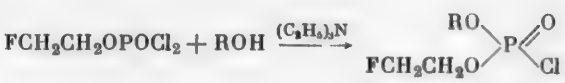
N. M. Gamper and L. F. Efimova

Institute of Organoelement Compounds, Academy of Sciences, USSR

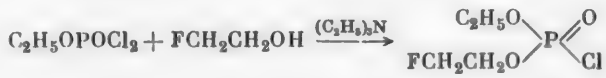
In a previous article [1] we described the preparation and testing of the insecticidal properties of some β-fluorinated esters of phosphorus acids. Since all the substances synthesized were found to be only weak insecticiddes, we continued the investigation of β-fluoroethyl derivatives amongst dialkylamides of phosphorus acids. For this purpose, we synthesized and tested ester-amides of the general formula:



The synthesis was accomplished by the following scheme:

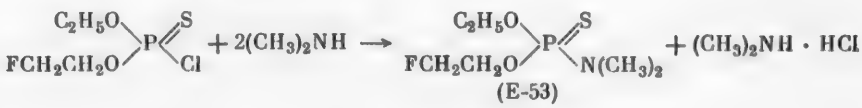


We prepared β-fluorodiethyl chlorophosphate, which was described previously [2], by a somewhat different method, namely from ethyl dichlorophosphate and β-fluoroethanol.



The alkyl β-fluoroethyl chlorophosphates obtained are presented in Table 1. Then, by reaction with dimethylamine, these substances were converted smoothly into the corresponding ester-amides.

The reaction of β-fluorodiethyl chlorothionephosphate with dimethylamine yielded β-fluorodiethyl dimethylamidothionephosphate (E-53).



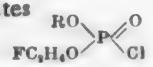
(E-53)

Table 2 gives the properties of alkyl β-fluoroethyl dimethylamidophosphates and β-fluorodiethyl dimethylamidothionephosphate.

The insecticidal properties of alkyl β-fluoroethyl dimethylamidophosphates (E-42, E-44 and E-45) and

β-fluorodiethyl dimethylamidothionephosphate (E-53) were studied. As previously [1], the compounds were used in the form of emulsions prepared from concentrates containing 30% of the active principle and 70% of OP-7. The contact action was investigated on the larvae of older muchnistyi chervets (Pseudococcus maritimus Ehr.) by spraying the insects. Experiments on the systemic action were carried out on larvae of the 2nd stage of the Italian grasshopper (Calliptamus italicus L.) by treating grain before sowing. The seed of spring wheat was sprinkled with 0.6% (on the active principle) of emulsions of the compounds, dried in air and sown in pots after

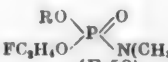
TABLE 1

Alkyl β-Fluoroethyl Chlorophosphates 

Substance No.	Meaning of R	B. p. (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield (in %)	Analysis results (in %) (calculated values are given in brackets)
E-40	CH_3	61.5° (1)	1.4140	1.3926	31.67	31.69	63	C 20.25, 20.30 (20.04); H 4.07, 4.05 (4.0)
E-41	C_2H_5	74.5 (1)	1.4160	1.3152	36.35	36.31	45	C 25.43, 25.41 (25.20); H 4.88, 5.0 (4.71)
E-43	iso-C_3H_7	65—66 (1)	1.4162	1.2488	41.11	40.93	44	P 14.98, 15.02 (15.14)
E-46	iso-C_4H_9	76—77 (1)	1.4220	1.2140	45.74	45.55	60	C 33.53, 33.28 (32.97); H 6.06, 6.27 (6.00)
E-21	FC_2H_4	130—131(1)	1.4060	1.4066	36.41	36.34	11	P 15.56, 15.31 (15.34)

1 day. Grasshopper larvae were put onto three-day old shoots of the wheat and left on them for 7 days. The results of the experiment were determined on the 7th day. The data obtained are presented in Table 3, which shows that the compounds tested had a very weak contact action for muchnistyi chervets. Thus, to reach 93-94% dead or paralyzed individuals, Thiophos had to be used in 0.025% concentration and the substance tested had to be in 0.5% of considerably higher concentrations. Of the two compounds similar in structure (E-53 and E-42), the derivative of amidothionephosphoric acid (E-53) was found to be slightly more active than the

TABLE 2

Alkyl β-Fluoroethyl Dimethylamidophosphates  (E-53) and β-Fluorodiethyl Dimethylamidothionephosphate (E-53)

Substance No.	Meaning of R	B.p. (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield (in %)	Analysis results (in %) (calculated values are given in brackets)
E-44	CH_3	65—66 (1)	1.4170	1.1954	39.05	39.21	85	C 32.09, 32.29 (32.43); H 10.54, 10.08 (10.27); P 7.34, 7.34 (7.57)
E-42	C_2H_5	62 (0.5)	1.4178	1.1449	43.79	43.83	93	C 36.53, 36.38 (36.18); H 7.85, 7.63 (7.53); P 7.46, 7.40 (7.04)
E-45	iso-C_3H_7	68 (1)	1.4169	1.1059	48.42	48.45	91	C 39.78, 39.34 (39.47); H 7.98, 7.83 (7.98)
E-47	iso-C_4H_9	75 (1)	1.4225	1.0882	53.06	53.07	94	C 41.78, 41.60 (42.28); H 8.36, 8.27 (8.43)
E-53	C_2H_5 (derivative of thiophosphoric acid)	68 (1)	1.4665	1.1482	51.84	51.40	84	C 33.40, 33.61 (33.51); H 7.15, 7.22 (7.03)

amidophosphoric acid derivative. Among the derivatives of amidophosphoric acid (E-42, E-45 and E-44), the ethyl compound (E-42) was more toxic than the isopropyl (E-45), while the isopropyl derivative was slightly more toxic than the methyl (E-44). The compounds tested were also weak insecticides by systemic action. Grasshopper larvae, fed on wheat shoots grown from seed treated with 0.6% emulsions of Mercaptophos, were 96.7% killed, while when the seed was treated with emulsions of the compound tested, the highest mortality of the grasshoppers was of the order of 31.7%.

TABLE 3

Activity against Insects by Contact and Systemic Action of some Ester-Amides of Phosphorus Acids Containing β-Fluoroethyl Groups (on the 7th day)

Substance No.	Muchnistyi chervets larvae		Grasshopper larvae	
	emulsion conc. (%)	no. of dead and paralyzed (in %)	emulsion conc. (in %)	mortality of larvae (in %)
E-53	0.5	94.8	0.6	—
E-42	0.5	83.1	0.6	6.7
E-45	0.5	76.8	0.6	28.3
E-44	0.5	71.6	0.6	31.7
Thiophos	0.025	93.3	—	—
Mercaptophos (mixture of isomers)	0.015	98.9	0.6	96.7

EXPERIMENTAL

Synthesis of alkyl β-fluoroethyl chlorophosphates. Methyl β-fluoroethyl chlorophosphate (E-40). With stirring, to an ether solution of 5.1 g of triethylamine was added first, 9.05 g of β-fluoroethyl dichlorophosphate and then 1.6 g of methyl alcohol. The reaction, which proceeded without the evolution of heat at the beginning of the experiment, required cooling of the flask after some time. Triethylamine hydrochloride was isolated in the theoretical amount. After removal of the ether, the residue was distilled.

Similarly, we obtained the ethyl, isopropyl and isobutyl β-fluoroethyl chlorophosphates (E-41, E-43 and E-46). The yields, constants and analysis data are presented in Table 1.

Di-β-fluorodiethyl chlorophosphate (E-21). 25.6 g of fluoroethanol was added to 30.7 g of phosphorus oxychloride. The rate of addition was regulated according to the reaction mixture temperature, which was kept at about 20°. The hydrogen chloride was removed in the cold with a stream of CO_2. The residue was vacuum distilled. Di-β-fluoroethyl chlorophosphate is a very unstable substance, which rapidly darkens on standing. The yield, constants and analysis data are presented in Table 1.

Synthesis of alkyl β-fluoroethyl dimethylamidophosphates. Methyl β-fluoroethyl dimethylamidophosphate (E-44). To a cooled ether solution of 2.5 g of dimethylamine was added 4.8 g of methyl β-fluoroethyl chlorophosphate. After the addition of methyl β-fluoroethyl chlorophosphate, the reaction mixture was stirred for another 1 hour. Dimethylamine hydrochloride was isolated in the theoretical amount. The ether was removed in the cold and the residue vacuum distilled.

Ethyl, isopropyl and isobutyl β-fluoroethyl dimethylamidophosphates (E-42, E-45 and E-47) were obtained similarly (see Table 2).

β-Fluorodiethyl dimethylamidothionephosphate (E-53). To an ether solution of 1.83 g of dimethylamine was added 4.2 g of β-fluorodiethyl chlorothionephosphate with stirring and cooling. Dimethylamine hydrochloride crystals precipitated rapidly. After removal of the ether, the residue was vacuum distilled. The yield, constants and analysis of the substance are presented in Table 2.

SUMMARY

1. Some alkyl β-fluoroethyl chlorophosphates and alkyl β-fluoroethyl dimethylamidophosphates were synthesized.

2. The substances obtained were found to be weak contact and systemic insecticides.

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ORTHOESTERS OF OXAMIC ACIDS

A. V. Kirsanov and V. P. Molosnova

Institute of Organic Chemistry, Academy of Sciences, Ukranian, SSR

Among the orthoesters of oxamic acids, up to the present time there has only been a report of the amide of trimethoxyacetic acid, which was obtained by R. Anschutz and J. Stiepel [1] by the scheme

$$CH_3OCOCOOCH_3 \xrightarrow{+PCl_5} CH_3OCOCCl_2OCH_3 \xrightarrow{+2NaOCH_3}$$
$$\longrightarrow CH_3OCOC(OCH_3)_3 \xrightarrow{+NH_3} NH_2COC(OCH_3)_3$$

The recently obtained amides of alkoxydichloroacetic acids [2], dimethylamides of alkoxydichloroacetic acids [3] and the dimethylamide of phenoxydichloroacetic acid [3] may be used as starting materials for the synthesis of orthoesters of oxamic and dimethyloxamic acids by the general scheme.

$$NH_2COCCl_2OR + 2NaOR' \longrightarrow 2NaCl + NH_2COC(OR)(OR')_2.$$

The amide of trimethoxyacetic acid, which was obtained previously by Anschutz and Stiepel [1], was obtained by the action of the amide of methoxydichloroacetic acid on sodium methylate. The properties of the compound obtained agreed with the data of Anschutz with the exception of the melting point. According to Anschutz' communication the amide of trimethoxyacetic acid melts at 118°, while this substance actually melts at 123-125°.

The action of the amides and dimethylamides of alkoxydichloroacetic acids on sodium arylates yielded orthoesters of oxamic and dimethyloxamic acids of the type $NH_2COC(OR)(OAr)_2$ and $(CH_3)_2NCOC(OAr)_2$, i. e., amides and dimethylamides of alkoxydiaroxyacetic acids. They were colorless crystalline compounds without smell, which were quite stable under normal conditions and hydrolyzed slowly by water at room temperature and more rapidly on heating. The amides and dimethylamides of alkoxydi-p-nitrodiphenoxyacetic acids were hydrolyzed more rapidly than the amides and dimethylamide of the corresponding alkoxydiphenoxyacetic acids. The dimethylamides of aloxydiaroxyacetic acids melted considerable below the unsubstituted amides of the corresponding alkoxydiaroxyacetic acids.

EXPERIMENTAL

Amide of trimethoxyacetic acid (trimethyl orthoester of oxamic acid) $NH_2COC(OCH_3)_3$. With vigorous stirring and cooling with ice-water, 0.06 mole of freshly prepared methoxydichloroacetamide was added in small portions to a solution of 0.12 mole of sodium methylate tin 70 ml of methanol. The reaction proceeded with the evolution of heat. When all the amide had been added, the mixture was heated and stirred on a water bath at 55-60° for 1 hour. When the mixture had been cooled, the sodium chloride was collected by filtration, boiled with 50 ml of methanol and again sucked off. The filtrates were combined, the methanol removed in vacuum and the residue recrystallized from a mixture of petroleum ether and benzene (1 : 1).

General method of preparing amides and dimethylamides of alkoxydiaroxyacetic acids $NH_2COC(OR)(OAr)_2$ and $(CH_3)_2NCOC(OR)(OAR)_2$. 0.02 mole of the amide or dimethylamide of the alkoxydichloroacetic acid was rapidly added with vigorous stirring to a mixture of 0.04 mole of sodium arylate and 25 ml of dioxane.

Amides and Dimethylamides of Alkoxydiaroxyacetic Acids of the Type $NH_2COC(OR)(OAr)_2$ and $(CH_3)_2NCOC(OR)(OAr)_2$

No.	Type of amide	R	Ar	Reaction temperature	Reaction time min.	Recrystallization substance, yield, %	Form of crystals	M. p.	Formula	N content (%) found	N content (%) calc	Solubility**** eth-anol	ether	petro-leum ether	CCl_4	ace-tone	C_6H_6
I*	Amide	CH_3	CH_3	—	—	45	Fine, lustrous needles	123—125°	$C_5H_{11}O_4N$	9.34***	9.40	±	+	—	—	+	—
II**	Amide	CH_3	C_6H_5	90°	30	60	Fine prisms	157—159	$C_{15}H_{15}O_4N$	5.26, 5.12	5.13	+	—	=	=	+	—
III	Amide	C_2H_5	C_6H_5	60	30	55	Fine, fluffy needles	113—115	$C_{16}H_{17}O_4N$	4.99, 4.97	4.88	—	+	—	—	+	—
IV	Amide	C_2H_5	$p\text{-}NO_2C_6H_4$	70	90	28	Fine prisms	193—194	$C_{16}H_{16}O_8N$	11.32, 11.39	11.40	—	=	=	=	+	—
V	Amide	$n\text{-}C_4H_9$	C_6H_5	50	40	52	Needles joined in bunches	108—110°	$C_{18}H_{21}O_4N$	4.53, 4.55	4.45	+	+	—	—	±	—
VI	Amide	$iso\text{-}C_4H_9$	C_6H_5	50	40	50	Fine prisms	122—124	$C_{18}H_{21}O_4N$	4.58, 4.53	4.45	+	—	—	—	+	+
VII	Dimethylamide	CH_3	C_6H_5	70	60	53	Coarse prisms	81—83	$C_{17}H_{19}O_4N$	4.76, 4.70	4.65	—	+	—	—	±	±
VIII	Dimethylamide	CH_3	$p\text{-}NO_2C_6H_4$	100	60	20	Fine prisms	175—177	$C_{17}H_{17}O_8N_3$	11.00, 10.96	10.74	—	=	=	—	±	—
IX	Dimethylamide	C_2H_5	C_6H_5	65	40	50	Coarse prisms	71—73	$C_{18}H_{21}O_4N$	4.54, 4.56	4.45	+	+	—	+	±	+
X	Dimethylamide	$n\text{-}C_4H_9$	C_6H_5	60	60	42	Fine prisms	73—74	$C_{20}H_{25}O_4N$	4.10, 3.97	4.08	+	+	—	+	±	+
XI	Dimethylamide	$iso\text{-}C_4H_9$	C_6H_5	60	60	40		70—72	$C_{20}H_{25}O_4N$	4.16, 4.34	4.08	+	+	—	+	±	+

* The reaction was carried out in methanol.

** The reaction was carried out in benzene.

*** Found %: OCH_3 60.64, 62.69. Calculated %: OCH_3 62.41.

**** Substance (I) was very readily soluble in water and all the rest of the amides were insoluble in water. All the amides were very readily soluble in dioxane. Meaning of symbols: (=) sparingly soluble at boiling point, (—) soluble at boiling point, (+) soluble at room temperature, (±) soluble at room temperature.

A reaction accompanied by the liberation of heat began immediately and the form of the precipitate and the color of the reaction mixture changed. When the evolution of heat ceased, the mixture was heated on a water bath at 50-90° for 30-90 minutes and then the sodium chloride removed by filtration or centrifuging and washed with hot dioxane. The yield of sodium chloride was 85-100%. The filtrates were combined and the dioxane removed in vacuum. The residue was colorless crystals mixed with a dark brown liquid or a thick brown liquid, which crystallized when solvent was added. The yield of the "crude"reaction products was close to 100%, but their purification involved great losses.

Treatment of "crude" amides and dimethylamides of alkoxydiaroxyacetic acids (see Table). The amount of solvent given are for 0.02 moles of starting amides of dimethylamides of alkoxydichloroacetic acids. The amide (I) was described above. Amide (II) was washed with water, dried and recrystallized from 20.0 ml of C_6H_6. Amide (III) was washed with water, dried and recrystallized from CCl_4 (4 × 25 ml) or dissolved in 20 ml of boiling ethanol, boiled with activated charcoal and filtered and 100 ml of water added to the filtrate. Amide (IV) was treated with 15 ml of ether, sucked free from solvent, dried, dissolved in 10 ml of dioxane and 10 ml of C_6H_6 added to the solution. Amides (V) and (VI) were boiled with 50 ml of ethanol, 200 ml of water added, the precipitate sucked off, dried and recrystallized from 30 ml of petroleum ether. Dimethylamide (VII) was washed with anhydrous ethanol (2 × 1 ml) and recrystallized from 3 ml of anhydrous ethanol, (VIII) was recrystallized from 120 ml of anhydrous ethanol and (IX) was dissolved in 20 ml of ethanol, 200 ml of a saturated aqueous solution of NaCl added and the precipitate sucked off after 2 hours, washed with water (3 × 15 ml), dried and recrystallized from 6 ml of anhydrous ethanol. If a seed was added, then dimethylamide (IX) crystallized after 10-12 hours. It was sucked off and washed with petroleum ether (2 × 1 ml) and 1 ml of alcohol. Substances (X) and (XI) were treated with 30 ml of a saturated aqueous solution of NaCl, sucked off after 1 hour, washed with water (2 × 15 ml), dried, washed with 1 ml of anhydrous ethanol and recrystallized from 2 ml of anhydrous ethanol.

SUMMARY

The action of sodium arylates on amides and dimethylamides of alkoxydichloroacetic acids yielded amides and dimethylamides of alkoxydiaroxyacetics acids (orthoesters of oxamic and dimethyloxamic acids).

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EXTENSION OF THE PHOSPHAZO REACTION

I. N. Zhmurova and A. V. Kirsanov

Institute of Organic Chemistry, Academy of Sciences, Ukrainian, SSR

At the present time, three methods are known for synthesizing phosphazo compounds. By G. Staudinger's method phosphazo compounds of the type $R_3P = NR'$, where R and R' are aryls or alkyls, are obtained by the action of tertiary phosphines on azides [1]. L. Horner and A. Gross studied the Staudinger reaction in detail [2] and M. I. Kabachnik and V. A. Galyarov considerably extended its application by using as the phosphorus-containing components trialkyl phosphites and esters of alkylphosphinic acids, which made it possible to obtain alkyldialkoxyphosphazoaryls of the type $Alk(Alk'O)_2P = NAr$. A. V. Kirsanov, G. I. Derkach and R. G. Makitra found that Staudinger's method could also be used to obtain triaroxyphosphazoaryls of the type $(ArO)_3 P = NCOAr'$ by the actionof appropriate azides on triphenyl phosphite [4]. F. Mann and E. Chaplin were the first to demonstrate the possibility of obtaining phosphazo compounds of the type $Ar_3P = NSO_2Ar'$ by the action of sodium salt of chloroamides of arylsulfonic acids on tertiary aromatic phosphines [5]. Several years later, A. V. Kirsanov et al. considerably extended the application of Mann and Chaplin's reaction and prepared a series of phosphazo compounds of very varied types [6]. In 1952, A. V. Kirsanov found a phosphazo reaction, which made it possible to obtain for the first time trichlorophosphazo compounds of the type $RN = PCl_3$, where R may be a wide variety of acyls ($So_2 <$, RSo_2-, $CO<$, $ArCo-$, CCl_3CO-, Ar_2PO-, etc.) [7]. Trichlorophosphazo compounds served as starting materials for the synthesis of various new types of phosphoric acid derivatives, including various triphenoxy- and trialkoxyphosphazo compounds [7]. V. I. Shevchenko et al. considerably extended the application of the phosphazo reaction by using as the phosphorus-containing components arylphosphorus tetrachlorides, which made it possible to obtain aryl aryldichlorophosphazosulfones of the type $(Ar)Cl_2P = NSO_2Ar$ and many of their derivatives [8]. K. A. Petrov and G. A. Sokol'skii obtained triphenoxyphosphazoethyl by the action of N-chlorodiethylamine on triphenyl phosphite [19].

A large number of different phosphazo compounds and their derivatives may be obtained by means of the phosphazo reaction, which proceeds practically quantitatively and makes it possible to obtain trichlorophosphazo compounds from very readily available and cheap starting materials. However, the phosphazo reaction, like the other two methods of obtaining phosphazo compounds, is far from universal. Thus, for example, the phosphazo reaction cannot be used to obtain phosphazo compounds of the type $\equiv P = NAr$, since the phosphazo reaction cannot be carried out with arylamines and phosphorus pentachloride. Therefore, trichlorophosphazoaryls of the type $Cl_3P = NAr$ were unknown up to now and trialkoxyphosphazoaryls were obtained only recently by M. I. Kabachnik and V. A. Galyarov from aryl azides and trialkyl phosphites [3]. Triaroxyphosphazoaryls of the type $(ArO)_3P = NAr$ were unknown up to now.

In the present work an attempt was made to extend the application of the phosphazo reaction so as to be able to use it for preparaing phosphazo compounds of the type $P = NAr$, in particular, triaroxyphosphazoaryls of the type $(ArO)_3P = NAr'$. In 1897 D. Gilpin reported that the action of phosphorus pentachloride on aniline hydrochloride yielded trichlorophosphazophenyl, $Cl_3P = NC_6H_5$, in the form of a "colorless sublimate". The author did not give the analysis of this substance or describe its properties [9]. Tests showed that Gilpin's data was not correct. Heating phosphorus pentachloride with aniline hydrochloride actually yielded a very small amount of a "colorless sublimate", but this sublimate consisted mainly of phosphorus pentachloride and did not contain trichlorophosphazophenyl. Thus, trichlorophosphazophenyl had not been prepared up to now and it would hardly be possible to obtain it in satisfactory yield from phosphorus pentachloride and aniline. It was therefore,

decided to replace phosphorus pentachloride by milder phosphorylating agents, namely, triphenoxyphosphorus dichloride and pentaphenoxyphosphorus. In this way one might hope to obtain directly from amines the corresponding triaroxyphosphazo compounds of the type $(ArO)_3P = NR$.

Triphenoxyphosphorus dichloride $(C_6H_5O)_2PCl_2$, was first obtained by R. Anschutz [10] by the action of chlorine on triphenyl phosphite. By the same method, triphenoxyphosphorus dichloride was obtained in recent years by D. Coe, S. Landauer and H. Rydon [11] and then by H. Rydon and B. Tonge [12]. The drawback of this method consists of the necessity for strict control of the amount of chlorine, since excess chlorine sharply lowers the yield. W. Autenrieth [13] obtained triphenoxyphosphorus dichloride by heating phenol with phosphorus pentachloride, but he was unable to isolate the product in a pure state.

A convenient method for the synthesis of triaroxyphosphorus dichlorides, which was applied for the first time in the present work, is the reaction of phosphorus pentachloride with triaryl phosphites by the scheme:

$$(ArO)_3P + PCl_5 \longrightarrow PCl_3 + (ArO)_3PCl_2$$

The reaction of triphenyl phosphite with phosphorus pentachloride proceeded with slight evolution of heat and was complete in a few minutes. Phosphorus trichloride was removed in vacuum and after 1 day, the triphenoxyphosphorus dichloride solidified as a crystalline mass with m. p. 76-80°. Rydon [11] gives m. p. 80-81° for purified triphenoxyphosphorus dichloride. Triphenoxyphosphorus dichloride is insoluble in ether, benzene and petroleum ether, but dissolves in acetone. It is very rapidly hydrolyzed by water and atmospheric moisture.

Pentaphenoxyphosphorus, $(C_6H_5O)_5P$, was first obtained by L. Anschutz by the scheme:

$$(C_6H_5O)_3PCl_2 + 2C_6H_5OH \longrightarrow 2HCl + (C_6H_5O)_5P$$

However, the reaction conditions were not given sufficiently clearly by the author. We carried out the reaction at 140-150° with subsequent removal of the hydrogen chloride in vacuum. After 1 day, the pentaphenoxyphosphorus formed solidified as a crystalline mass with m. p. 80-92°. Pentaphenoxyphosphorus dissolves in ether and carbon tetrachloride, but is insoluble in benzene, dioxane and petroleum ether. It is hydrolyzed very rapidly by water and atmospheric moisture.

As was noted above, it was not possible to achieve a phosphazo reaction on aromatic and aliphatic amines with phosphorus pentachloride. With aromatic amines, triphenoxyphosphorus dichloride and pentaphenoxyphosphorus formed triphenoxyphosphazoaryls by the schemes (A) and (B).

$$(C_6H_5O)_3PCl_2 + ArNH_2 \longrightarrow 2HCl + ArN{=}P(OC_6H_5)_3 \quad (A)$$
$$(C_6H_5O)_5P + ArNH_2 \longrightarrow 2C_6H_5OH + ArN{=}P(OC_6H_5)_3 \quad (B)$$

The reaction with amides proceeded analogously.

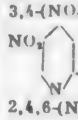
$$(C_6H_5O)_3PCl_5 + AcNH_2 \longrightarrow 2HCl + AcN{=}P(OC_6H_5)_3 \quad (C)$$
$$(C_6H_5)_5P + AcNH_2 \longrightarrow 2C_6H_5OH + AcN{=}P(OC_6H_5)_3 \quad (D)$$

Triphenoxyphosphorus dichloride reacted with amides and amines at 130-160°. This reaction was especially convenient for amides of sulfonic acids. In the case of amines, it was necessary to introduce into the reaction 2 additional moles of base for binding the hydrogen chloride or to add 2 moles of a tertiary amine. The reaction formed a mixture of the amine hydrochloride and the triphenoxyphosphazoaryl.

It was more convenient to use pentaphenoxyphosphorus for preparing triphenoxyphosphazoaryls. The reaction proceeded at 140-160° in a vacuum of 5-10 mm. The phenol formed as a result of the reaction then distilled. When the phenol stopped distilling, the reaction was complete. Usually about 80% of the theoretical amount of phenol distilled. Carrying out the reaction at normal pressure, without removing the phenol by distillation, considerably lowered the yield. This made it difficult to react pentaphenoxyphosphorus with amides and amines which boil below 140° in vacuum. Table 1 gives the yields, melting points and analysis results for triphenoxyphosphazoaryls and Table 2 gives the yields and melting points of triphenoxyphosphazoacyls.

TABLE 1

Triphenoxyphosphazoaryls ArN = P(OC$_6$H$_5$)$_3$

Substance No.	Ar	Obtained by scheme	Yield (in %)	M. p.	Composition of molecules	N content (in %) found	N content (in %) calc.
I	C_6H_5	A B	57 62	Liquid	$C_{24}H_{20}O_3NP$	3.22, 3.20	3.49
II	4-$NO_2C_6H_4$	B	62	76—78°	$C_{24}H_{19}O_5N_2P$	6.24, 6.30	6.28
III	2,4-$(NO_2)_2C_6H_3$	B	80	77—79	$C_{24}H_{18}O_7N_3P$	8.49, 8.41	8.55
IV	3,4-$(NO_2)_2C_6H_3$	B	—	Liquid	—	—	—
V		B	60	58—60°	$C_{28}H_{19}O_5N_2P$	9.88, 9.70	9.40
VI	2,4,6-$(NO_2)_3C_6H_2$	B	72	98—100	$C_{24}H_{17}O_9N_4P$	10.38, 10.41	10.44

*B. p. 254-257° (8 mm).

**Would not distill without decomposition.

The known triphenoxyphosphazoacyls (VII-X) were identified by the melting points of mixtures with authentic substances. Triphenoxyphosazoaryls (I-VI) were obtained for the first time. Triphenoxyphosphazophenyl (I) was also obtained from phenylazide and triphenyl phosphite (cf. [1] and [3]) by the scheme

$$C_6H_5N_3 + (C_6H_5O)_3P \longrightarrow N_2 + C_6H_5N{=}P(OC_6H_5)_3$$

It should be noted that phenyl azide reacts with triphenyl phosphite much more slowly than trialkyl phosphites. The reaction of trialkyl phosphites with phenyl azide lasts for about half an hour [3], while with triphenyl phosphite, 3 days are required. The substance obtained was identical with the condensation product of aniline and triphenoxyphosphorus dichloride or pentaphenoxyphosphorus. Triphenoxyphosphazophenyl was a colorless liquid with b.p. 254 – 257° (8 mm), which was soluble in benzene, chloroform, ether, acetone, dioxane and carbon tetrachloride.

TABLE 2

Triphenoxyphosphazoacyls AcN = P(OC$_6$H$_5$)$_3$

Substance No.	Ac	Obtained by scheme	Yield (in %)	M. p.	Literature
VII	$C_6H_5SO_2$	C D	63 80	85—86°	[15]
VIII	$SO_2[N{=}P(OC_6H_5)_3]_2$	C D	63 50	132—134	[16]
IX	$(C_6H_5O)_2PO$	D	44	72—74	[17]
X	$(C_6H_5O)_2PS$	D	80	96—98	[17]

Triphenoxyphosphazonitrophenyls (II, III and IV) were light yellow, cryststalline substances, which were readily soluble in benzene, chloroform, dioxane, carbon tetrachloride and hot alcohol, but insoluble in petroleum ether. Triphenoxyphosphazo-3,4-dinitrophenyl was a liquid, which did not distill without decomposition and therefore we were unable to obtain it in a pure state.

According to the communication of M. I. Kabachnik and V. A. Galyarov [3], the hydrolysis of trialkoxyphosphazophenyls with water at room temperature proceeds very slowly (1.5 months). Triphenoxyphosphazoaryls

(I-V) (in contrast to trialkoxyphosphazophenyls) were rapidly hydrolyzed with the formation of the diphenyl esters of the corresponding arylamidophosphoric acids by the scheme

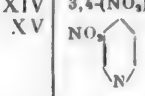
$$(C_6H_5O)_3P{=}NAr + H_2O \longrightarrow C_6H_5OH + (C_6H_5O)_2PONHAr,$$

which is a reliable indication of their structure and a method of identification. Triphenoxyphosphazophenyl was hydrolyzed most readily of all and was hydrolyzed quantitatively in a few minutes in contact with 50% ethanol at room temperature. In contact with 50% ethanol at room temperature, triphenoxyphosphazo-p-nitrophenyl was not hydrolyzed appreciably after 12 hours, but was hydrolyzed completely after 1 hour's boiling with 50% ethanol. Under the same conditions, triphenoxyphosphazo-2,4-dinitrophenyl was hardly hydrolyzed. The triphenoxyphosphazoaryls (I-V) were hydrolyzed rapidly and quantitatively when boiled with aqueous ethanol to which a few drops of concentrated hydrochloric acid had been added. When hydrolyzed, triphenoxyphosphazo-2,4,6-trinitrophenyl (VI) decomposed at the nitrogenphosphorus bond and gave picramide. It should be noted that all the triphenoxyphosphazoaryls (I-VI) were hydrolyzed very much more readily in the impure state than the pure substances. When the crude reaction mixtures were shaken with water, complete hydrolysis occured very rapidly. This is probably explained by the catalytic effect of side products and impurities. The yields, melting points and analysis results for the diphenyl esters of arylamidophosphoric (acids of the type) $(C_6H_5O)_2PONHAr$ are presented in Table 3.

Compounds (XI-XV) were colorless, crystalline substances, which were soluble in chloroform, dioxane, acetone, hot benzene and alcohol and insoluble in water, ether and petroleum ether. Substances (XII-XV)had weakly expressed acidic properties; they dissolved in alkali, sodium carbonate and ammonia on gentle heating. Compound (XI) was insoluble in alkali.

TABLE 3

Diphenyl Esters of Arylamidophosphoric Acids $(C_6H_5O)_2PONHAr$

Substance No.	Ar	Yield (in %)	M. p.	Literature	Composition of molecule	N content (in %)	
						found	calc.
XI	C_6H_5	80	129—130°	[13]	—	—	—
XII	$4\text{-}NO_2C_6H_4$	98	146—148	[18]	—	—	—
XIII	$2,4\text{-}(NO_2)_2C_6H_3$	92	144—146	—	$C_{18}H_{14}O_7N_3P$	9.73, 9.78	10.12
XIV	$3,4\text{-}(NO_2)_2C_6H_3$	42*	143—145	—	$C_{18}H_{14}O_7N_3P$	9.99, 9.87	10.12
XV		40	188—190	—	$C_{17}H_{14}O_5N_3P$	11.47, 11.32	11.32

* Calculated on crude triphenoxy-3,4-dinitrophosphazophenyl.

W. Autenrieth reacted triphenoxyphosphorus dichloride with aniline [13] and obtained the diphenyl ester of phenylamidophosphoric acid (XI), which, in his opinion, was formed by the scheme.

$$(C_6H_5O)_3PCl_2 + 4C_6H_5NH_2 \longrightarrow \left[(C_6H_5O)_2P\begin{matrix}OC_6H_5\\NHC_6H_5\\NHC_6H_5\end{matrix}\right] \longrightarrow$$

$$\longrightarrow (C_6H_5)_2NH + (C_6H_5O)_2PONHC_6H_5$$

Autenrieth isolated neither the intermediate product nor the diphenylamine. Actually, the action of triphenoxyphosphorus dichloride on aniline yields triphenoxyphosphazophenyl, but Autenrieth was unable to isolate it as the reaction mixture was treated with dilute hydrochloric acid; this hydrolyzed the triphenoxyphosphazophenyl to the diphenyl ester of phenylamidophosphoric acid. Actually, the presence proceeded by the scheme

$$(C_6H_5O)_3PCl_2 + 3C_6H_5NH_2 \longrightarrow (C_6H_5O)_3P{=}NC_6H_5 \xrightarrow{+H_2O} (C_6H_5O)_2PONHC_6H_5.$$

EXPERIMENTAL

Triphenoxyphosphorus dichloride. To 0.1 mole of triphenyl phosphite was added 0.1 mole of phosphorus pentachloride. The mixture gave off heat and after 5-10 minutes, the phosphorus pentachloride had dissolved completely. The reaction mixture was heated on an oil bath in a vacuum of 5-10 mm first at 100° and finally at 130-140° to remove the phosphorus trichloride. Complete removal of the phosphorus trichloride was checked by periodic weighing. Usually the phosphorus trichloride was removed completely after 30-40 minutes. The residual thick, slightly yellowish liquid changed after 1 day into a crystalline mass with m. p. 76-78° (ina sealed capillary). The yield was theoretical.

Pentaphenoxyphosphorus. A mixture of 0.1 mole of triphenoxyphosphorus dichloride and 0.2 mole of phenol was heated on an oil bath at 140-150° for 2 hours; slight evolution of hydrogen chloride occurred. The mixture was then heated for 2-3 hours at 150-160° in a vacuum of 3-5 mm, so as to remove the hydrogen chloride completely. Complete removal of the hydrogen chloride was checked by periodic weighing. After 1 day the pentaphenoxyphosphorus solidified as a crystalline mass, melting at 80-90° in a sealed capillary. Anschutz [14] reported m. p. 46-52° for pentaphenoxyphosphorus, which is not correct. The yield was theoretical.

Triphenoxyphosphazophenyl. A. 0.1 mole of triphenoxyphosphorus dichloride and 0.3 mole of dry aniline were heated on an oil bath at 120-130° for 2 hours. Then 50.0 ml of dry benzene was added to the reaction mixture and the aniline hydrochloride removed by filtration and washed with dry benzene. The benzene was removed and the triphenoxyphosphazophenyl vacuum distilled. A fraction boiling at 254-257° (8 mm) was collected.

B. 0.1 mole of pentaphenoxyphosphorus and 0.1 mole of dry aniline were heated on an oil bath at 140-150° for 2 hours and then for 1 hour in a vacuum of 5 mm, while the temperature was gradually raised to 180°. When phenol (77%) no longer distilled, the residue was vacuum distilled. A fraction boiling over the range 254-257° (8 mm) was collected.

C. To a solution of 0.03 mole of triphenyl phosphite in 25.0 ml of dry ether was added 0.03 mole of phenyl azide. The gentle evolution of gas bubbles began immediately and was complete after 3 days. After removal of the ether, the triphenoxyphosphazophenyl was vacuum distilled. The b. p. was 254-257° (8 mm) and the yield 80%. On hydrolysis with water (see below), triphenoxyphosphazophenyl, obtained by methods A, B and C, yielded the same product, namely, the diphenyl ester of phenylamidophosphoric acid with m. p. 129-130°.

Triphenoxyphosphazonitrophenyls (II, IV and VI, Table 1). Equimolecular amounts of the appropriate nitroaniline and pentaphenoxyphosphorus were heated on a n oil bath at 140-160° in a vacuum of 5 mm for 30-40 minutes, until the distillation of phenol ceased. The crude triphenoxyphosphazonitrophenyls were thick, orange liquids. Substance (II, III and VI) crystallized on cooling and scratching with a glass rod, while compound (IV) could not be crystallized. Substances (II) and (VI) were ground with anhydrous alcohol and substance (III) with anhydrous isopropyl alcohol, sucked off and dried in vacuum. The triphenoxyphosphazonitrophenyls purified in this way melted 3-4° below the recrystallized ones. They were finally purified by recrystallization from anhydrous alcohol.

Triphenoxyphosphazo-5-nitropyridyl-2 (V, Table 1). 2-Amino-5-nitropyridine was condensed with pentaphenoxyphosphorus as described above. After removal of the phenol, absolute ether was added to the cooled residue. The ether solution was filtered free from unreacted 2-amino-5-nitropyridine, the ether removed in vacuum and the crystalline residue treated in the cold with anhydrous isopropyl alcohol, filtered and dried in vacuum.

Phenyl triphenoxyphosphazosulfone (VII, Table 2). A. A mixture of 0.01 mole of triphenoxyphosphorus dichloride and 0.01 mole of benzenesulfonamide was heated on an oil bath at 160° until the liberation of hydrogen chloride ceased (about 1.5 hours). Water was added to the cooled reaction mixture. An oil was precipitated and this rapidly crystallized. The crystals were sucked off, washed with 2% sodium hydroxide solution, water, and alcohol and recrystallized from alcohol.

B. 0.01 mole of benzenesulfonamide and 0.01 mole of pentaphenoxyphosphorus were heated on an oil bath at 140-150° in a vacuum of 5 mm for 30 minutes. During this time 80% of the theoretical amount of phenol distilled over. Further processing was the same as in the previous experiment.

Bis-triphenoxyphosphazosulfone (VIII, Table 2) was obtained by condensation of sulfamide with triphenoxyphosphorus dichloride or pentaphenoxyphosphorus similarly to phenyl triphenoxyphosphazosulfone.

Diphenyl triphenoxyphosphazophosphate (IX, Table 2) was obtained by heating equimolecular amounts of diphenyl phosphamate and pentaphenoxyphosphorus at 140-150° and 5 mm for 30 minutes. When the distillation of phenol (78%) ceased, the reaction mixture was dissolved in hot benzene. The solution was cooled, filtered free from unreacted diphenyl phosphamate and the diphenyl triphenoxyphosphazophosphate precipitated from the benzene solution with petroleum ether.

Diphenyl triphenoxyphosphazothionephosphate (X, Table 2) was obtained similarly to the previous one. After the distillation of phenol (82%) had ceased, the reaction mixture was treated with 50% methanol and the crystalline precipitate formed was collected by filtration and recrystallized from methanol.

Diphenyl phenylamidophosphate (XI, Table 3). To 0.01 mole of triphenoxyphosphazophenyl was added 20.0 ml of 50% ethyl alcohol. After 2-3 minutes, the liquid triphenoxyphosphazophenyl was converted into the crystalline amidoester. The reaction was accompanied by slight evolution of heat. The crystals were collected by filtration and recrystallized from alcohol.

Diphenyl nitrophenylamidophosphates (XII-XIV, Table 3). 0.01 mole of the appropriate triphenoxyphosphazoaryl was dissolved with heating in the minimal amount of alcohol. To the solution were added several drops of 10% hydrochloric acid and the solution boiled under reflux for 15 minutes. On cooling, the ester of nitrophenylamidophosphoric acid formed precipitated in a crystalline state. The precipitate was sucked off, washed with alcohol and dried. The substances obtained in this way did not require further purification. For the hydrolysis of triphenoxyphosphazonitrophenyls with aqueous alcohol, see the general section.

Diphenyl 5-nitropyridyl-2-amidophosphate (XV, Table 3). 0.01 mole of triphenoxyphosphazo-5-nitropyridyl-2 was dissolved with heating in 10.0 ml of alcohol. On cooling, several drops of 10% hydrochloric acid were added to the alcohol solution and the mixture left at room temperature for 4 hours. 10.0 ml of water and several drops of an aqueous ammonia solution (to a neutral reaction) were added. The precipitated crystals were collected by filtration, washed with alcohol and recrystallized from alcohol.

SUMMARY

1. The action of phosphorus pentachloride on triarylphosphites yielded triaroxyphosphorus dichlorides.

2. It is possible to use not only phosphorus pentachloride, but also pentaphenoxyphosphorus and triphenoxyphosphorus dichloride as phosphorus-containing components in the phosphazo reaction.

3. The action of triphenoxyphosphorus dichloride or pentaphenoxyphosphorus on aromatic amines yielded triphenoxyphosphazoaryls and their properties are described.

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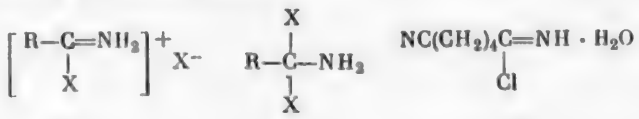
PRODUCTS OF THE INTERACTION OF ADIPONITRILE WITH HYDROGEN CHLORIDE AND THEIR HYDROLYSIS

E. N. Zil'berman and A. E. Kulikova

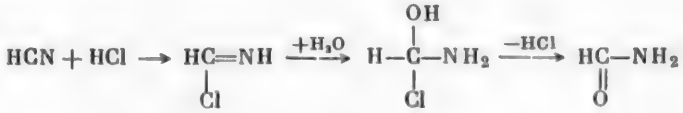
Until recently it was almost generally accepted that nitriles form both mono- and dihydrohalides with hydrogen halides. The former were ascribed the structure of nitrilium slats [1] or iminohalides [2] and the latter, that of hydrohalides of nitrilium salts [1] or amidohalides [2]. However, in work on the reactions of a series of nitriles with hydrogen halides it was shown [3] that only dihydrohalides were formed and that these were either hydrohalides of imonium halides of carboxylic acids (A) or amidohalides (B) with the former structure preferred. In connection with the reaction of products formed



(A) (B) (C)

from nitriles and hydrogen halides with water, in the literature [2] Hantzsch's [1] point of view is held and according to this only hydrolysis may occur with the formation of the original nitrile. The reaction of dinitriles with hydrogen halides is not considered in the literature. There is only a report [4] that the addition of 1 mole of hydrogen chloride for 1 mole of adiponitrile forms an iminochloride, which is converted by water into the hydrate of the iminochloride (C); the properties of the latter were not given. The formation of an iminochloride contradicts the data presented above [3], according to which addition products of 1 molecule of hydrogen halide and 1 molecule of nitrile do not exist. The formation of hydrate (C) is also incomprehensible.

The hydrolysis of nitriles into amides has been studied by many authors [5]. On the basis of an investigation of the hydrolysis of hydrocyanic acid in the presence of concentrated hydrohalic acids, the following reaction mechanism was put forward [6]:



All the stages in this scheme and, above all, the formation of the iminochloride are doubtful.

In the present work, an investigation was made of the reaction of adiponitrile with hydrogen chloride. It was particularly interesting to determine whether one nitrile group could be hydrochlorinated selectivity. Then it was necessary to determine the nature of the compounds formed from hydrochlorinated nitriles and and water, since at the very beginning of the work it was found that Hantzsch's [1] statement that only the starting nitriles were formed was incorrect. Actually, when hydrochlorinated nitriles were introduced into ice water, hydrolysis occurred with the evolution of nitrile and HCl, but when small amounts of water were introduced into an ether solution of the reaction products of nitriles with HCl, an extremely stable precipitate formed. Finally, since it was possible to isolate the reaction products of adiponitrile with hydrogen chloride and water, it was worth while to examine the hydrolysis mechanism of nitriles in the presence of concentrated hydrohalic acids.

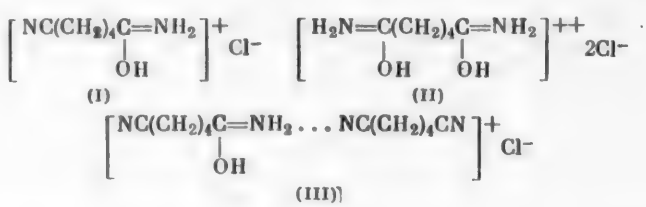
To ether solutions of adiponitrile and hydrogen chloride, taken in various ratios, were added various amounts of water (Table 1). It was found that compounds precipitated in which the adiponitrile, water and hydrogen chloride were present in the ratios 1 : 1 : 1 (I), 1 : 2 : 2 (II)and 2 : 1 : 1 (III). The preferential formation

TABLE 1

Reaction of Adiponitrile with Hydrogen Chloride and Water

Expt. No.	Molecular ratio in reaction mixture	Chlorides obtained	Yield on hydrolysis of chlorides (in moles)		
			adiponitrile	δ-cyanovaleramide	adipamide
1	2 : 2 : 1	(III)	0.50	0.50	None
2	1 : 1 : 1	(I) + (III)	0.33	0.65	None
3	1 : 2 : 1	(I)	None	0.98	None
4	1 : 3 : 2	(I) + (II)	None	0.08	0.85
5	1 : 4 : 2	(II)	None	None	0.99

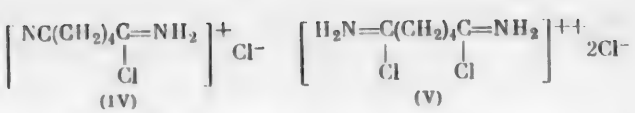
of one of them depended on the amount of the reagents in the starting mixture. When dissolved in water and neutralized, compounds (I) and (II) were quantitatively converted into δ-cyanovaleramide and adipamide; in concentrated sulfuric acid solution, (I) and (II) reacted with sodium nitrite [7] with the formation of δ-cyanovaleric and adipic acids. On the basis of these reactions it can be considered that compounds (I) and (II) are salts in which the amides exist in the lactone form, i. e. substances (I) and (II) are chlorides of the imonium hydrins of the corresponding carboxylic acids. Evidently they are analogous to the compounds formed by dissolving amides in concentrated sulfuric acid [1]. The least stable of the products we obtained from the inter-



action of adiponitrile, hydrogen chloride and water, compound (III), has a more complicated structure. Dissolving it in water and subsequent neutralization yielded equivalent amounts of adiponitrile and δ-cyanovaleramide and in benzene (III) lost 1 molecule of adiponitrile and was converted into (I). Apparently (III) is a molecular compound of (I) and adiponitrile,and its instability is explained by the weakness of the hydrogen bond. It should be noted that Experiment 2 yielded a mixture of compounds (I) and (III) and not a compound with structure (C) [4].

The data in Table 1 show that half of the nitrile groups in adiponitrile react with hydrogen chloride only when the molecular ratio between the reagents reaches 1 : 2; all the nitrile groups react with hydrogen chloride when the molar ratio between the adiponitrile and hydrogen chloride is not less than 1 : 4. From this it follows that 2 molecules of hydrogen chloride add to 1 nitrile group and that the primary products of hydrochlorination of adiponitrile are [3] the chloride of the imonium chloride of δ-cyanovaleric acid (IV) and the dichloride of the diimonium chloride of adipic acid (V).

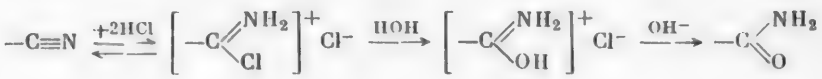
The selectivity of the hydrochlorination of adiponitrile attracts attention. The nitrile group in adiponitrile is considerably more reactive than that in the chloride of the imonium chloride (IV). Therefore, on hydrochlorination, adiponitrile is first exclusively converted into compound (IV). The dichloride of the di-



(IV) (V)

imonium chloride (V) begins to form only when all the adiponitrile had disappeared from the reaction mixture. The reduction of the nucleophilic properties of the nitrogen of the nitrile group in compound (IV) (in comparison with adiponitrile) is hardly connected with the negative induction effect caused by the presence of the chloride of the immonium chloride grouping in the molecule since the functional groups in (IV) are separated by four methylene groups. Apparently the reduction in the nucleophilic properties of the nitrile nitrogen in (IV) is explained by intramolecular interaction (due to a hydrogen bond) between the nitrogen of the nitrile group and the hydrogen of the imonium group. The loss of reactivity of the nitrile group in (IV) may also be explained by its interaction with the hydrogen atom of the methylene group in the α-position with respect to the imonium-chloride group. This hypothesis is supported by the results of measuring the dipole moments of a series of dinitriles, according to which the structure of adiponitrile differs considerably from the linear [8], and the capacity of adiponitrile to form a five-membered ring comparatively readily [9].

On the basis of the above considerations, it can be postulated that the formation of amides by hydrolysis in the presence of concentrated hydrohalic acids proceeds by the following scheme



First, 2 molecules of hydrogen halide are added to the nitrile and as a result the chloride of an imonium chloride is formed and the chlorine atom in the latter is then replaced by a hydroxyl group. Hydrolysis of the chloride of the imonium hydrin yields the amide. To confirm the above scheme, a series of experiments (Table 2) were carried out in which water was added to the reaction products of adiponitrile and HCl, at various periods of time after the HCl had been passed into the adiponitrile. It was found that if the water was added immediately after preparation of an ether solution of adiponitrile and hydrogen chloride, the yield of (I) was low; a mixture of (I) and its molecular compound with adiponitrile (III) was precipitated. If the water was added when the

TABLE 2

Effect of Interaction Time of Adiponitrile and Hydrogen Chloride on the Yield of the Chloride of the Imonium Hydrin of δ-Cyanovaleric Acid (Starting mixture: 5.4 g of adiponitrile and 3.65 g of hydrogen chloride in 20 ml of ether. 0.9 g of water was added)

Standing period of starting mixture before addition of water (in hours)	(I) and (III) obtained		Yield of (I) and (III) calculated on (I) (in % of theoretical)
	(in g)	Cl (in %)	
0	5.8	17.7	58.1
1	6.8	18.5	72.4
2	7.1	20.3	82.2
4	7.9	21.6	96.6
5	8.1	21.75	99.8
20	8.1	21.8	100.0

starting mixture had been kept for a definite time, the amount of unreacted adiponitrile became less and the yield of (I) increased. Thus, in the hydrolysis of nitriles in the presence of concentrated acids, the formation of chlorides of imonium chlorides is actually the primary reaction.

In conclusion it should be noted that the syntheses of δ-cyanovaleramide and adipamide described above

are convenient methods of preparing these substances in almost theoretical yields. In the literature there is only one preparative method described for obtaining δ-cyanovaleramide in a 31% yield [10]. The reaction of the chloride of the imonium hydrin of δ-cyanovaleric acid (I) with sodium nitrite is also of preparative interest as a new method of synthesizing δ-cyanovaleric acid.

EXPERIMENTAL*

Synthesis of the chloride of the imonium hydrin of δ-cyanovaleric acid (I), δ-cyanovaleramide and δ-cyanovaleric acid (Exp. 3). With stirring and cooling to 0°, 7.3 g (0.2 mole) of dry hydrogen chloride was passed into a heterogeneous mixture of 10.8 g (0.1 mole) of adiponitrile and 20 ml of dry ether. When this mixture was cooled to -20° it deposited a white precipitate, but we were unable to isolate it as it immediately decomposed in air. The mixture was kept for 4 hours in the cold and then 1.8 g (0.1 mole) of water was added. After 20 hours, the white precipitate was collected by filtration, washed with dry ether and dried in a desiccator over $CaCl_2$ to give 15.8-16.2 g (98-100%) of (I). (I) was very hygroscopic, unstable in air, could be stored in a desiccator for 2 months without noticeable decomposition, was soluble in water and insoluble in organic solvents, softened at 0-78° and had m. p. 160-165° (decomp.).

Found %: Cl 21.7; N (total) 17.1; N (amide) [11] 8.4. $C_6H_{11}ON_2Cl$. Calculated %: Cl 21.8 (total) N (total) 17.2; N (amide) 8.6.

Experiments to determine the effect of prolonged interaction of adiponitrile with hydrogen chloride on the formation of the chloride of the imonium hydrin of δ-cyanovaleric acid (Table 2) were carried out similarly with the difference that the reagent concentrations were a factor of 2 less and the precipitate was collected by filtration 40 hours after the addition of water. The yield of useful product in this series of experiments was determined from the weight of the precipitate and the chlorine content of the latter by means of the following formula

$$\frac{g \cdot a \cdot 100}{G \cdot 21.8},$$

where g is the weight of the precipitate (in g), a the chlorine content of the precipitate (in %), G the theoretical yield of (I) (in g) and 21.8 the chlorine content of (I) (in weight %).

40 g of (I) was dissolved in 60 ml of water and neutralized to methyl orange with sodium carbonate. The solution obtained was evaporated and the residue treated with ethyl acetate. The solvent was removed from the extract and the residue was 30.6 g [98% of theoretical on (I)] of δ-cyanovaleramide with m.p. 67° (from a mixture of ethyl ether and ethyl acetate, 1 : 1). A mixed melting point [12] was not depressed.

15 g of (I) was dissolved in 100 g of 90% sulfuric acid with cooling to 0°. With stirring and cooling to 0°, a solution of 15 g of $NaNO_2$ in 20 ml of water was slowly added to the solution obtained. The reaction mixture was then heated to 90°, when there was a vigorous evolution of a colorless gas. When cool, the solution was extracted 3-4 times with small portions of cyclohexanol. The extract was dried with anhydrous Na_2SO_4 and distilled. We obtained 7 g (60%) of δ-cyanovaleric acid (b. p. 176° at 8 mm), which was identical with the product obtained previously [12] and was hydrolyzed to adipic acid when boiled with 40% sulfuric acid.

Synthesis of the dichloride of the diimonium hydrin of adipic acid (II) and adipamide (Exp. 5). The synthesis of (II) was similar to the preparation of (I). To 10.8 g of adiponitrile and 20 ml of dry ether was added 14.6 g (0.4 mole) of dry hydrogen chloride. Cooling the solution to -3° yielded a white precipitate, which could not be isolated due to its instability in air. Twenty hours after the addition of 3.6 g (0.2 mole) water, the white precipitate was collected by filtration, washed with ether and dried in a desiccator; we obtained 22 g (100%) of (II). The product was sparingly soluble in cold water and insoluble in organic solvents. It was unstable in air, could be stored in a desiccator without noticeable decomposition and melted with decomposition at 186-195°.

Found %: Cl 32.2; N 12.7. $C_6H_{14}O_2N_2Cl_2$. Calculated %: Cl 32.7; N 12.9.

* With the participation of K. K. Ish.

10 g of (II) was added to 25 ml of water and neutralized to methyl orange with 10% alkali. The white precipitate (5.1 g) was collected by filtration and washed with water. Concentration of the mother solution yielded a further 1.5 g of substance. The total yield of adipamide was 6.6 g (99%) and the product had m.p. 220°. A mixed melting point was not depressed.

Synthesis of the molecular compound of the chloride of the imonium hydrin of δ-cyanovaleric acid with adiponitrile (III) and isolation of its hydrolysis products (Exp. 1). The synthesis of (III) was similar to the preparation of (I) and (II). From 10.8 g of adiponitrile, 3.6 g (0.1 mole) of dry hydrogen chloride and 0.9 g (0.05 mole) of water we obtained 10 g (74%) of (III). The compound softened at 48-60° and melted with decomposition at 115-130°.

Found %: Cl 13.0; N (total) 21.0; N (amide) 4.95. $C_{12}H_{19}ON_4Cl$. Calculated %: Cl 13.1 N (total) 20.7; N (amide) 5.17.

(III) was even less stable in air than (I) and (II), but could be stored in a desiccator without noticeable decomposition and was soluble in water. Careful washing of 9.2 g of (III) with dry benzene yielded 3.75 g of adiponitrile and 5.45 g of (I).

Found %: Cl 21.6. $C_6H_{11}ON_2Cl$. Calculated %: Cl 21.8.

15 g of (III) was dissolved in 25 ml of water and neutralized with sodium carbonate, when the solution separated into layers. The aqueous layer was extracted several times with ethyl acetate. The extracts and the upper layer were dried with calcium chloride and the solvent removed. Treatment of the thickened residue with benzene yielded 7.2 g (50%) of δ-cyanovaleramide with m. p. 67°. A mixed melting point was not depressed. The benzene solution was washed with a small amount of water and removal of the solvent yielded 6.9 g (50%) of adiponitrile.

SUMMARY

1. It was shown that in the hydrochlorination of adiponitrile, at first 2 molecules of hydrogen chloride are added selectively to 1 nitrile group with the formation of the chloride of the imonium chloride of δ-cyanovaleric acid. Continuation of the hydrochlorination forms the dichloride of the diimonium chloride of adipic acid.

2. On the example of adiponitrile derivatives, it was found that the interaction of equivalent amounts of chloride of imonium chlorides and water gives quantitative yields of the chlorides of imonium hydrins, which are converted to amides of the corresponding acids by hydrolysis and neutralization.

3. A mechanism is proposed for the hydrolysis of nitriles in the presence of concentrated hydrohalic acids.

4. New methods were developed for obtaining high yields of δ-cyanovaleramide, δ-cyanovaleric acid and adipamide.

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SYNTHESIS OF THIAZOLIDONE DERIVATIVES OF BIOLOGICAL INTEREST

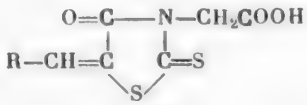
XI. RHODANINE-3-ACETIC ACID AND ITS DERIVATIVES

N. M. Turkevich and M. I. Ganitkevich

Lvov Medical Institute

The derivatives of 3-methylrhodanine, which we described in a previous communication [1], are of definite biological interest, but their insolubility in water considerably hinders their pharmacological testing. Due to this, we turned our attention to rhodanine-3-acetic acid and its derivatives since the presence of a carboxyl group in their molecules makes it possible to obtain water-soluble salts readily.

Rhodanine-3-acetic acid (A) was first synthesized in 1908 by Korner [2] by Miolati's method [3]. We synthesized rhodanine-3-acetic acid by the same method and obtained a substance which we condensed with



(A)

benzaldehyde, cinnamaldehyde, anisaldehyde, m-nitrobenzaldehyde, salicyaldehyde and furfural. The substance obtained were yellow crystalline preparations of various shades, which were readily soluble in alkali solutions.

The data from our spectrophotometric investigations show that the carboxyl groups as R-chromophores do not change the position of the intense absorption maxima in the UV-region and mainly affect the absorption intensity only. Thus, with identical substituents R in position 5, the absorption curves of 3-methylrhodanine derivatives are very reminiscent of the absorption curves of rhodanine-3-acetic acid (see Fig. 1). The thione bands (250-275 mμ) are of high intensity; however, the maxima in this region, with the exception of that of unsubstituted rhodanine-3-acetic acid, are poorly expressed and usually change into inflections or disappear completely. In absorption intensity, this band corresponds to the analogous band of semicarbazide [4] and thiourea [5].

The amide band (286-301 mμ) is characterized by a lower absorption intensity than that of the thione band with the absorption maximum strongly expressed for unsubstituted rhodanine-3-acetic acid and its 5-cinnamylidene and 5-furfurylidene derivatives (see Fig 1). For typical 5-arylidene derivatives, these maxima are almost converted into inflections.

The longwave edge of the absorption curve (ϵ 1000) of rhodanine-3-acetic acid is at about 340 mμ. For 5-derivatives it is shifted towards longer wavelengths by 60 mμ and more, due to the presence of an intense K-band (370-401 mμ). This band is connected with the presence of the conjugated chromophores =C–C=C–R, where the radical R has a further two (furfurylidene group), three (arylidene group) or four (cinnamylidene group) –C=C– grouping. The K-band is characterized by the most strongly expressed absorption maximum, whose intensity, with the exception of that of the 5-salicylidene derivative (see Fig. 2), exceeds 20,000.

The absorption spectra of the ammonium salts of rhodanine-3-acetic acid and its derivatives are presented in Figs. 3 and 4. Replacement of the H atom in the carboxyl group by the NH_4 group hardly changes the positions

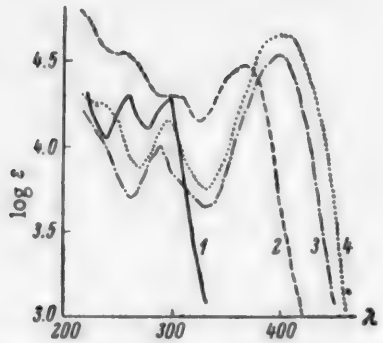


Fig. 1. Absorption spectrum curves. 1) rhodanine-3-acetic acid, 2) 5-m-nitrobenzylidenerhodanine-3-acetic acid, 3) 5-furfurylidenerhodanine-3-acetic acid, 4) 5-cinnamylidenerhodanine-3-acetic acid.

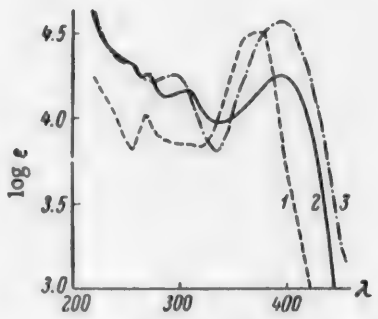


Fig. 2. Absorption spectrum curves. 1) 5-benzylidenerhodanine-3-acetic acid, 2) 5-salicylidenerhodanine-3-acetic acid, 3) 5-p-anisylidenerhodanine-3-acetic acid.

of the maxima and minima on the absorption curves. A change in the absorption intensity is mainly observed in the thione and amide bands only.

Investigations carried out in the Pharmacology Department of the Lvov Medical Institute (Prof. A. A. Gavrilyuk et al.) showed that some of the substances we synthesized had definite antispasmodic activity.

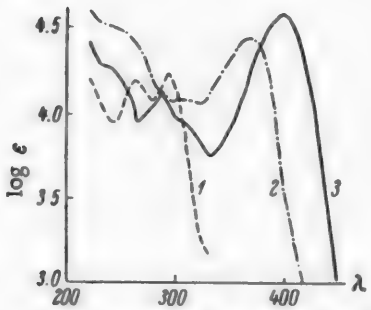


Fig. 3. Absorption spectrum curves. 1) ammonium rhodanine-3-acetate, 2) ammonium 5-m-nitrobenzylidenerhodanine-3-acetate, 3) ammonium 5-furfurylidenerhodanine-3-acetate.

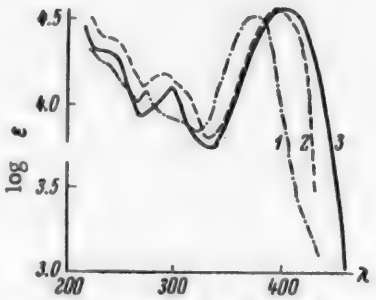


Fig. 4. Absorption spectrum curves. 1) ammonium 5-benzylidenerhodanine-3-acetate, 2) ammonium 5-p-anisylidenerhodanine-3-acetate, 3) ammonium 5-cinnamylidenerhodanine-3-acetate.

EXPERIMENTAL

We obtained rhodanine-3-acetic acid from glycine, carbon disulfide and monochloroacetic acid. Its melting point (146-147°) corresponded to literature data [2]. For the preparation of 5-substituted derivatives, 0.01 mole of rhodanine-3-acetic acid was boiled in a flask under reflux for 2 hours with 0.01 mole of the appropriate aldehyde in the presence of anhydrous sodium acetate and glacial acetic acid. The cooled reaction mixture was diluted with water and the condensation product collected by filtration and recrystallized from alcohol

or glacial acetic acid. The melting points of the 5-benzylidene (241°) and 5-m-nitrobenzylidene derivatives (253-254°) corresponded to literature data [2]. The introduction of dry ammonia into the acetone solution of the substances obtained precipitated the ammonium salts in the cold in the form of water-soluble, crystalline products. The preparations we synthesized for the first time are presented in the Table.

Compound	Yield (in %)	M. p.	Calc. (%)			Found (%)		
			C	H	N	C	H	N
5-Cinnamylidene-rhodanine-3-acetic acid	82	229—231°	55.06	3.63	4.58	55.43	3.79	4.68
5-p-Anisylidene-rhodanine-3-acetic acid	81	241	50.47	3.59	4.53	51.23	3.90	4.56
5-Furfurylidenerhodanine-3-acetic acid	88	207—209	44.60	2.62	5.20	45.23	2.93	5.29
Ammonium rhodanine-3-acetate	97	191—192 (decomp.)			13.45			13.71
Ammonium 5-benzylidenerhodanine-3-acetate	85	236—237 (decomp.)			9.45			9.73
Ammonium 5-m-nitrobenzylidene-rhodanine-3-acetate	91	234—235 (decomp.)			12.31			12.72
Ammonium 5-cinnamylidenerhodanine-3-acetate	76	193—194 (decomp.)			8.69			8.66
Ammonium 5-p-anisylidenerhodanine-3-acetate	70	242—243 (decomp.)			8.58			9.16
Ammonium 5-furfurylidenerhodanine-3-acetate	85	203—205 (decomp.)			9.79			10.23

We carried out the spectrophotometric investigation with an SF-4 spectrophotometer. The light source was a low-voltage arc hydrogen lamp, VSFU-3. Alcohol solutions of the substances examined at a concentration of 1 mg/100 ml were used.

SUMMARY

1. Spectrophotometric investigations were made of rhodanine-3-acetic acid and its 5-substituted derivatives and also of their ammonium salts.

2. Rhodanine-3-acetic acid is characterized by two absorption maxima in the thione (250-275 mμ) and amide (286-301 mμ) bands. These maxima are not characteristic of the condensation products of rhodanine-3-acetic acid with aldehydes and in some cases they disappear, while a K-band (370-401 mμ) appears with strongly expressed absorption maxima.

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S-DERIVATIVES OF THIOUREA

I. SYNTHESIS OF N-ACETYL- AND N,N-DIETHYL-2,3-DIISOTHIURONIUM PROPYLAMINE

V. M. Fedoseev, S. P. Kovalenko, A. B. Silaev and

An. N. Nesmeyanov

Moscow State University

Many S-derivatives of thiourea are biologically active substances including anesthetics, antibacterial agents, insecticides and agents for the chemical protection of organisms from the harmful effect of radioactive radiation. Salts of 2-aminoethylisothiuronium and 3-aminopropylisothiuronium have a high prophylactic protective effect against radiation sickness [1].

We were interested in analogs of these substances, namely derivatives of 2,3-diisothiuronium propylamine, containing two isothiuronium groups and one amino group (free or substituted). Many substances containing two isothiuronium groups are described, but they are all alkylidenediisothiuroniums, which do not contain other functional groups. An exception is the methyl ester of 9,10-diisothiuronium stearic acid [2], but in this compound the ester grouping is so far separated from the isothiuronium groups that it has hardly any effect on them and thus, this compounds differs little from alkylidenediisothiuroniums. The first compounds containing two isothiuronium groups and another functional group (in this case amino) on neighboring carbon atoms are the compounds we describe.

The dibromide of N,N-diethyl-2,3-diisothiuronium propylamine hydrobromide was obtained by scheme 1 and the dibromide of N-acetyl-2,3-diisothiouronium propylamine by scheme 2.

Scheme 1

$$CH_2{=}CHCH_2Br \xrightarrow{HN(C_2H_5)_2} CH_2{=}CHCH_2N(C_2H_5)_2 \cdot HBr \xrightarrow{Br_2}$$

$$\xrightarrow{Br_2} CH_2BrCHBrCH_2N(C_2H_5)_2 \cdot HBr \xrightarrow{2S=C(NH_2)_2}$$

$$\xrightarrow{2S=C(NH_2)_2} HN{=}C(NH_2 \cdot HBr){-}S{-}CH_2{-}CH(CH_2N(C_2H_5)_2 \cdot HBr){-}S{-}C(NH_2 \cdot HBr){=}NH$$

Scheme 2

$$CH_2{=}CHCH_2Br \xrightarrow{KSCN} CH_2{=}CHCH_2NCS \xrightarrow{CH_3COOH}$$

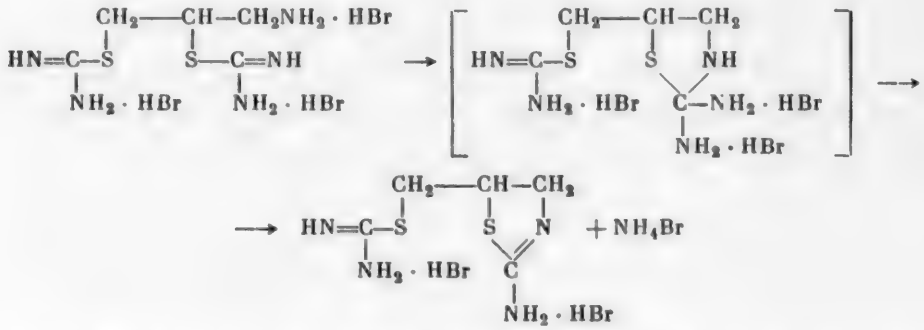
$$\xrightarrow{CH_3COOH} CH_2{=}CHCH_2NHCOCH_3 \xrightarrow{Br_2}$$

$$\xrightarrow{Br_2} CH_2BrCHBrCH_2NHCOCH_3 \xrightarrow{2S=C(NH_2)_2} HN{=}C(NH_2 \cdot HBr){-}S{-}CH_2{-}CH(CH_2NHCOCH_3){-}S{-}C(NH_2 \cdot HBr){=}NH$$

An attempt to synthesize the dibromide of 2,3-diisothiuronium propylamine hydrobromide from 2,3-dibromopropylamine hydrobromide and thiourea yielded a substance of a different composition from that of the

desired compound. As is known [3], in the case of 2-aminoethylisothiuronium, partial cyclization occurs under certain conditions with the formation of 2-aminothiazoline.

It is possible that under our conditions a similar conversion occurs to a large extent and leads to the formation of 2-amino-5-isothiuroniummethylthiazoline.



The analysis data of the compound obtained and its picrate agree well with the values calculated for the formula of the bromide hydrobromide and for the dipicrate of 2-amino-5-isothiuroniummethylthiazoline.

For biological testing it was important to prepare labeled derivatives of 2,3-diisothiuronium propylamine. For this purpose we synthesized thiourea, labeled with the radioactive isotope of sulfur, S^{35}, by the method in [4] with some changes. The synthesis of the labeled substances did not differ essentially from the synthesis of the inactive substances.

EXPERIMENTAL

Synthesis of Dibromide of N,N-Diethyl-2,3-diisothiuronium Propylamine Hydrobromide

Allyldiethylamine. This product was obtained from allyl bromide and diethylamine [5]. The use of a 3-fold excess of diethylamine improved the yield (from 30 to 40%). Allyldiethylamine was obtained in better yield (52%) by the following method. With vigorous stirring, 1 mole of anhydrous potassium carbonate was added to 1 mole of allyl bromide. The suspension was heated to boiling and 3 moles of diethylamine were added to it dropwise. The mixture was boiled for 6 hours, cooled and filtered. The filtrate was fractionated. The b. p. was 107-110°.

N,N-diethyl-2,3-dibromopropylamine. This compound is not described in the literature. Its synthesis was similar to that of 2,3-dibromopropylamine [10]. We obtained 217 g (80%) of the substance. The colorless crystals had m. p. 89-90° (from ethanol).

Found %: C 23.97, 23.99; H 4.73, 4.56; N 3.98, 4.17. $C_7H_{15}NBr_2$. Calculated %: C 23.73; H 4.52; N 3.96.

Dibromide of N,N-diethyl-2,3-diisothiuronium propylamine hydrobromide. 14.16 g of N,N-diethyl-2,3-dibromopropylamine hydrobromide and 6.00 g of thiourea were heated for 12 hours in 40 ml of butanol at 80° (at higher temperatures, partial decomposition of the reaction product was observed). The colorless, oily reaction product began to precipitate after 4 hours heating and then rapidly solidified. At the end of the reaction, the mixture was cooled and the precipitate collected and recrystallized twice from a mixture of acetone and ethanol (1 : 1). The colorless crystals had m. p. 183-184°. They were readily soluble in water and ethanol, less so in methanol and butanol, and insoluble in acetone and ether. The yield was 17.5 g (82%).

Found %: C 21.13, 21.22; H 4.99, 4.97; N 13.41, 13.48; Br 47.33, 47.09. $C_9H_{24}N_5Br_3S_2$. Calculated %: C 21.35; H 4.78; N 13.84; Br 47.36.

Synthesis of Dibromide of N-Acetyl-2,3-diisothiuronium Propylamine

Allyl isothiocyanate. This substance was obtained from allyl bromide and potassium thiocyanate with subsequent isomerization [6]. The b. p. was 42-46° (12 mm) and the yield 55%.

Allylacetamide. A mixture of equimolecular amounts of ally isothiocyanate and acetic acid (98%) was boiled for 14 hours [7]. The b. p. was 107-112° (15 mm) and the yield 65%.

N-Acetyl-2,3-dibromopropylamine. This product was obtained by bromination of allylacetamide in absolute carbon tetrachloride by Chiari's method [8] and in an absolute benzene medium. In both cases the yield was almost quantitative. The product was not purified.

Dibromide of N-acetyl-2,3-diisothiuronium propylamine. A solution of 8.00 g of N-acetyl-2,3-dibromopropylamine in 15 ml of dioxane was added dropwise to a solution of 4.65 g of thiourea in 60 ml of boiling dioxane. A viscous, oily, yellow product rapidly precipitated. The mixture was boiled for 4.5 hours. When heating was stopped, the dioxane was decanted and the residue twice treated with boiling acetone. We obtained 10.37g (83%) of a white crystalline substance. The m. p. was 192-193.5° (from methanol). The substance was readily soluble in water and hot methanol, difficultly so in ethanol, and insoluble in ether, dioxane and acetone.

Found %: C 20.72, 20.67; H 3.89, 3.95; Br 38.59, 38.88. $C_7H_{17}ON_5Br_2S_2$. Calculated %: C 20.45; H 4.17; Br 38.87.

The dipicrate of N-acetyl-2,3-diisothiuronium propylamine was precipitated from aqueous solution with picric acid. M. p. 208-209° (from water).

Found %: C 32.13, 32.22; H 3.06, 3.04. $C_{19}H_{21}O_{15}N_{11}S_2$. Calculated %: C 32.25; H 2.99.

Reaction Between Thiourea and 2,3-Dibromopropylamine Hydrobromide

Allylamine was obtained in 82% yield by hydrolysis of allyl isothiocyanate [9]. 2,3-Dibromopropylamine hydrobromide was obtained in 98% yield by bromination of allylamine in slightly acid aqueous solution [10].

14.9 g of 2,3-dibromopropylamine hydrobromide and 7.6 g of thiourea were heated at 80° in 85 ml of butanol. A white precipitate began to form after 2 hours. After being heated for 20 hours, the mixture was cooled and the precipitate collected. We obtained 13 g (74%, calculated on 2-amino-5-isothiuroniummethylthiazoline) of a crystalline substance. The m. p. was 218-220° (from ethanol). The substance was readily soluble in water and hot methanol, less so in ethanol and butanol and insoluble in acetone and ether.

Found %: C 17.31, 17.13; H 3.41, 3.63; N 15.52, 15.54; Br 45.20, 45.32. $C_5H_{12}N_4Br_2S_2$. Calculated %: C 17.05; H 3.41; N 15.91; Br 45.41.

The picrate of the product was precipitated with an aqueous solution of picric acid. The m. p. was 270° (decomp.).

Found %: C 31.45, 31.28; H 2.67, 2.73; N 21.24, 21.30. $C_{17}H_{16}O_{14}N_{10}S_2$. Calculated %: C 31.48; H 2.47; N 21.60.

Similar results were obtained in experiments in which a 2-fold excess of thiourea was used.

Chromatographic Analysis

To control the rate of reaction of thiourea with the corresponding N-derivatives of 2,3-dibromopropylamine and also to determine the purity of the substances obtained, we made use of paper chromatography. The mobile solvent was the organic layer of a mixture of butanol, acetic acid and water (4 : 1 : 5). The chromatograms were developed with Dragendorff's reagent ($KBiI_4$) or a 10% solution of copper sulfate. Dragendorff's reagent showed thiourea (yellow spot), the other starting materials and the reaction products (light red spots). When a chromatogram was treated with copper sulfate solution and then heated in a drying cupboard, thiourea and N-acetyl-2, 3-dibromopropylamine did not appear, while the other substances appeared as black spots. The R_f values are given in the table.

Synthesis of Substances Labeled with S^{35}

Thiourea. 0.4 g of sodium sulfide (43%), containing S^{35}, mixed with 2.2 g of inactive barium sulfide, 0.8 g of freshly prepared cyanamide [11], 2.4 g of ammonium bicarbonate and traces of sulfur, were shaken with 30 ml of water for 8 hours at 25-30°. Subsequent operations were according to the procedure in [4]. The yield of crude product was 1.05 g (83%). The crude product was recrystallized from ethanol. We isolated 0.63 g of pure product, which was diluted with 3.28 g of inactive thiourea and recrystallized from ethanol. We obtained 2.84 g of thiourea with a specific activity of $5.1 \cdot 10^6$ dis./ min. per g.

R_f Values (ascending method) of the Starting Material and Products

Starting material	Rf	Reaction product	R_f
2,3-Dibromopropylamine	0.53	2-Amino-5-isothiuronium-methylthiazoline*	0.23
N,N-Diethyl-2,3-dibromopropyl-amine	0.69	N,N-Diethyl-2,3-diisothiuronium propylamine	0.20
Thiourea	0.50	N-Acetyl-2,3-diisothiuronium propylamine	0.22

Dibromide of N,N-diethyl-2,3-diisothiuronium propylamine hydrobromide. 3.54 g of N,N-diethyl-2,3-dibromopropylamine hydrobromide and 1.52 g of thiourea of the given specific activity were heated in 27 ml of butanol at 80° for 13 hours. The product was isolated and purified as described for the inactive preparation. The yield was 3.82 g (75%). The specific activity was $1.5 \cdot 10^6$ dis./ min. per g.

Dibromide of N-acetyl-2,3-diisothiuronium propylamine. A solution of 1.89 g of N-acetyl-2,3-dibromopropylamine in 25 ml of dioxane was added dropwise to a solution of 1.09 g of thiourea in 25 ml of boiling dioxane. The mixture was boiled for 9 hours. The product was isolated and purified as described for the inactive preparation. The yield was 2.31 g (77%). The specific activity was $1.8 \cdot 10^6$ dis./ min. per g.

Samples for determining the specific activity of the labeled substances obtained were prepared by depositing exact amounts from methanol solutions onto standard aluminum trays and measured on an end-window counter with a mica window 2.3 mg/ cm^2 thick.

SUMMARY

Two new S-derivatives of thiourea were synthesized, namely, the dibromide of N,N-diethyl-2,3-disothiuronium propylamine hydrobromide and the dibromide of N-acetyl-2,3-diisothiuronium propylamine. The same substances labeled with the radioactive isotope of sulfur, S^{35}, were prepared.

It was established that the reaction between 2,3-dibromopropylamine hydrobromide and thiourea in butanol solution at 80° did not lead to the formation of the dibromide of 2,3-diisothiuronium propylamine hydrobromide. It is surmised that under these conditions the bromide of 2-amino-5-isothiuroniummethylthiazoline hydrobromide was obtained.

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* Supposed reaction product.

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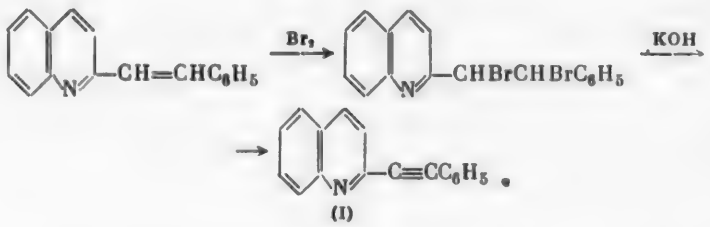
ADDITIONS TO SALTS OF 2-PHENYLACETYLENYLQUINOLINE

A. I. Kiprianov and G. G. Dyadyusha

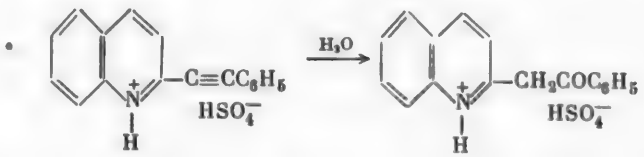
Kiev State University

2-Phenylacetylenylquinoline (I) was described* by Scheunig and Winterhalder [1] in 1928. These authors obtained it as an intermediate product in the synthesis of 2-phenacylquinoline. The starting material used was 2-styrylquinoline, which was converted into the dibromide and then into 2-phenylacetylenylquinoline by the action of alcoholic alkali.



(I)

This acetylene, exactly like a series of other analogous acetylenes of the quinoline and pyridine series, readily added water with the formation of a high yield of the phenacyl derivative [1, 2]. Since the reaction with water proceeded in 60-70% sulfuric acid, the water was apparently added to the salt of the base and not to the base.

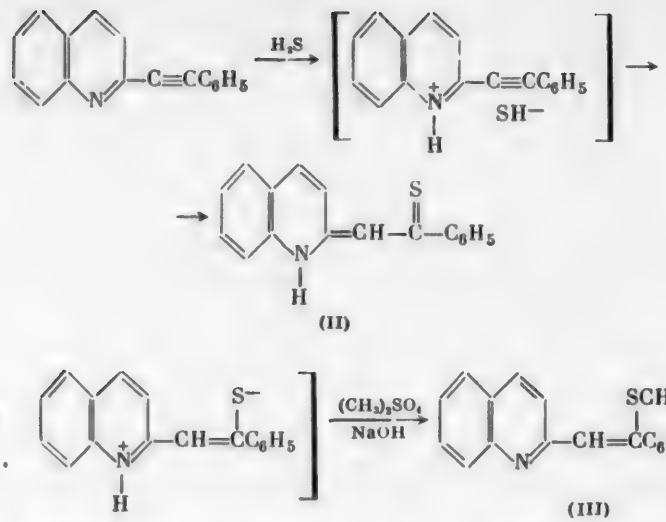


Thus, the positive charge on the nitrogen atom of the quinoline nucleus activates the triple bond for the addition of water as a nucleophilic reagent. Other additions with acetylenes of a similar nature have not been studied up to now.

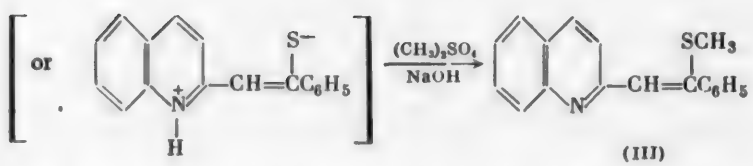
We established that 2-phenylacetylenylquinoline added hydrogen sulfide in alcohol solution with the formation of the thiobenzoyl derivative (II), which we then converted into α-methylmercaptostyrylquinoline (III) by the action of dimethyl sulfate in an alkaline solution. It is probable that the salt of the base and not the base reacted with hydrogen sulfide in this case.

On the basis of its optical properties, we ascribed the structure of 2-thiobenzoylmethylene-1,2-dihydroquinoline (II) and not that of thiophenylacylquinoline to the addition product of hydrogen sulfide and 2-phenylacetylenylquinoline. This product gave an intense orange alcohol solution while the thiophenacyl derivative

*With the incorrect melting point of 101° instead of 63°.



(II)



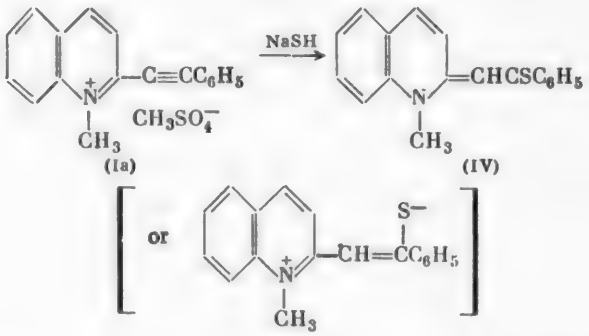
(III)

should be colorless. The light absorption curve of an alcohol solution of the addition product of hydrogen sulfide and phenylacetylenylquinoline was similar in form and the position of the absorption maximum (490 mμ) to the absorption curve of N-methyl-2-thiobenzoylmethylene-1,2-dihydroquinoline (IV); absorption maximum at 510 mμ).

We were unable to add other nucleophilic reagents to phenylacetylenylquinoline under the conditions of its reaction with water. In a strongly acid medium, amines are converted into salts and lose their capacity for addition. Substances with active methyl or methylene groups are only nucleophilic like amines in an alkaline medium and do not add to salts of phenylacetylenylquinoline either.

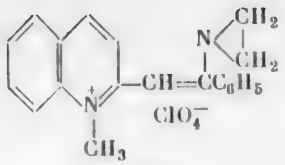
However, by the action of dialkyl sulfates or p-toluenesulfonic esters, 2-phenylacetylenylquinoline may be converted into quaternary salts, which are quite stable in alkaline solutions. We obtained such salts and found that they were capable of adding various nucleophilic reagents at the triple bond.

The action of sodium hydrosulfide on the methyl methosulfate of 2-phenylacetylenylquinoline (Ia) gave orange-red N-methyl-2-thiobenzoylmethylene-1,2-dihydroquinoline (IV).

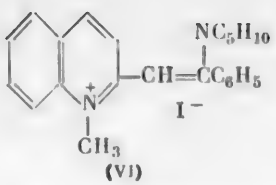


The action of ethyleneimine, piperidine and aniline on the same salt [Ia] yielded the corresponding addition products (V), (VI) and (VII).

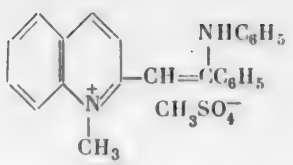
Acetoacetic ester and benzoylacetone were added to the methyl methosulfate of phenylacetylenylquinoline in alcohol solution in the presence of triethylamine with the formation of the dark red crystalline products (VIII) and (IX).



(V)

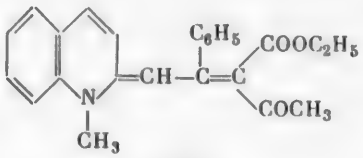


(VI)

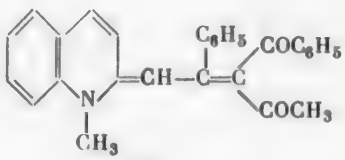


(VII)

We then found that like acetoacetic ester and benzoylacetone, nitrogen heterocycles containing active methyl or methylene groups readily added to quaternary salts of phenylacetylenylquinoline in the presence of triethylamine. The result was the formation of cyanine dyes of symmetrical or unsymmetrical structure, con-

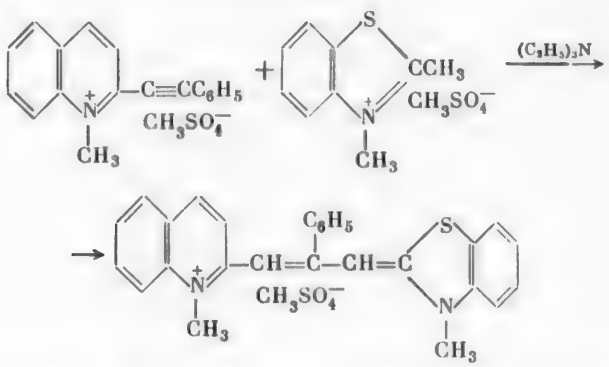


(VIII)



(IX)

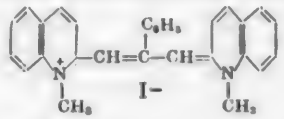
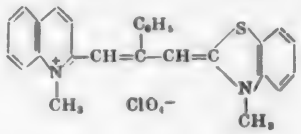
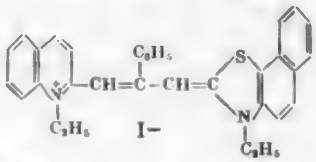
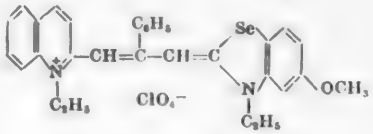
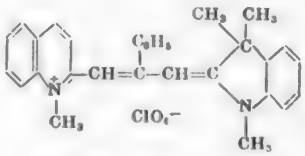
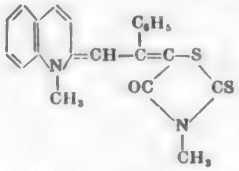
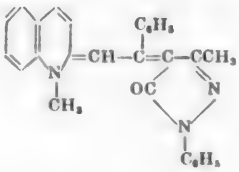
taining a phenyl group in the β-position of the polymethylene chain. As an example, we present the reaction of the methylmethosulfate of 2-phenylacetylenylquinoline with the quaternary salt of 2-methylbenzthiazole.



The formation of dyes by this type of reaction proceeds with satisfactory ease, without heating, simply by mixing together alcohol solutions of the reagents and for the most part, with high yields. In this connection the new method of synthesizing cyanine dyes with phenyl groups in the polymethylene chromophore is preferable to other methods of introducing aryl radicals into the chromophore of cyanines [3].

The table gives theformulas of the carbocyanines and merocyanines, we synthesized from phenylacetylenylquinoline, their absorption maxima in alcohol solutions and also the absorption maxima of the corresponding dyes without phenyl groups in the chain.

In the table, one's attention is attracted by the considerable shift in the absorption maximum (20-50 mμ) of all the dyes containing a phenyl group in the chromophore, in comparison with the dyes not containing this group. It is known that a phenyl in the meso-position of thiacarbocyanines has almost no effect on the position of the absorption maximum. According to van Dormael [8], this is explained by the fact that in thiacarbocyanines a phenyl group in the meso position does not have sufficient space to lie in the plane of the benzthiazole nuclei. It is turned perpendicular to it and due to this, it is prevented from affecting the light absorption. As Brooker et al. showed [9], in quinocarbocyanines there is even less space in the meso-position for a substituent than in thiacarbocyanines; therefore, a phenyl group even in a position perpendicular to the plane of the dye molecule produces such serious steric hindrance that the quinoline nuclei are partly forced out of coplanarity. This produces a shift in the absorption maximum towards the long wave region of the spectrum.

Compound No.	Formula of dye	Absorption maximum (in mμ)	
		dye synthesized (in alcohol solution)	corresponding dye without a phenyl group in the chain
(X)		648	604 (in CH_3OH [4])
(XI)		603	578 (N,N'-diethylcyanine; in CH_3OH [4])
(XII)		618	597 (N,N'-diethylcyanine; in CH_3OH [5])
(XIII)		616	
(XIV)		596	550 (N-ethyl-N'-methylcyanine; in CH_3OH [6])
(XV)		598, 568	568 (N,N'-diethylmerocyanine [7])
(XVI)		545	

EXPERIMENTAL

2-Phenylacetylenylquinoline (I). 65 g of 2-styrylquinoline dibromide were heated for 1 hour on a water bath with stirring with a solution of 25 g of potassium hydroxide in 160 ml of anhydrous alcohol. The alcohol was then evaporated on the water bath, the residue poured into 1 liter of cold water and the precipitate washed with water and recrystallized from methyl alcohol with water added. The yield was 24.4 g (64%) and the m. p. 63°; the melting point did not change after repeated recrystallizations (according to data in [1], m. p. 101°). The infrared spectrum showed absorption bands at 2230 and 2220 cm^{-1}, which are characteristic of acetylene derivatives. The ultraviolet absorption spectrum of 2-phenylacetylenylquinoline in alcohol was extremely complex and there were seven absorption bands in the region from 220 to 350 mμ; λ_{max} 344, 330, 322, 317, 275, 259 and 248 mμ (lg ε 4.26, 4.27, 4.21, 4.21, 4.40, 4.35 and 4.34) It differed considerably from the absorption spectrum of 2-styrylquinoline in alcohol, which has two broad absorption bands : λ_{max} 328 and 283 mμ (lg ε 4.35 4.39) [9].

Found %: N 6.33, 6.38. $C_{17}H_{11}N$. Calculated %: N 6.11.

Five quaternary salts of 2-phenylacetylenylquinoline were prepared. The N-methyl methosulfate (Ia) precipitated when an equimolecular mixture of base and dimethyl sulfate in toluene solution was kept for several days. After recrystallization from alcohol, it formed yellowish leaflets with m. p. 123° (with decomp.).

In alcohol solution, it had λ_{max} 379 mμ (lg ε 4.49) and 261 mμ (lg ε 4.34), and an inflection at about 285 mμ (lg ε 4.00). The N-ethyl ethosulfate was an uncrystallizable oil, which darkened on standing. The N-methyl p-toluenesulfonate (Ib) was obtained by fusing the base with methyl p-toluenesulfonate. Grinding the dark melt with acetone and ether yielded a white powder with m.p. 214° (with decomp.). The N-methyl perchlorate (m. p. 224°) and the N-ethyl perchlorate (m. p. 160°) were obtained by precipitation with sodium perchlorate from alcohol solutions of the appropriate alkyl sulfates.

2-Thiobenzoylmethylene-1,2-dihydroquinoline (II). A solution of 0.5 g of (I) in 5 ml of alcohol was saturated with hydrogen sulfide at 70°. After cooling, the liquid was sucked off and the precipitate washed with alcohol. The yield was 0.51 g (88%). The product crystallized from alcohol as red needles with m. p. 174.5°. In alcohol solution the substance had λ_{max} 491, 317, 284 and 228 mμ (lg ε 4.33, 4.08, 4.05 and 4.44); in chloroform, λ_{max} 497, 320 and 287 mμ (lg ε 4.42, 4.11 and 4.00); in alcohol in the presence of sodium hydroxide, λ_{max} 409 and 332 mμ (lg ε 4.18 and 3.86) and in the presence of sulfuric acid, λ_{max} 395 mμ.

Found %: S 12.10, 12.24. $C_{17}H_{13}NS$. Calculated %: S 12.17.

2-α-Methylmercaptostyrylquinoline (III). With stirring, 0.15 g of dimethyl sulfate and 0.1 g of sodium hydroxide were added to a solution of 2 g of the previous compound in 5 ml of alcohol. The decolorized solution was diluted with water and the precipitated oil extracted with ether. After evaporation of the ether, the product crystallized in flat, colorless prisms. The yield was 0.16 g (76%). After recrystallization from methanol, the substance had m. p. 61°; in alcohol solution it had λ_{max} 348 mμ (lg ε 4.21) and in the presence of acid, λ_{max} 401, 280 and 248 mμ (lg ε 4.37, 3.98 and 4.17).

Found %: S 11.60, 11.56. $C_{18}H_{15}NS$. Calculated %: S 11.56.

p-Methyl-2-thiobenzoylmethylene-1,2-dihydroquinoline (IV). With stirring, a solution of 0.6 ml of concentrated hydrochloric acid in 10 ml of methanol was added to a solution of 1.5 g of crystalline sodium sulfide nonahydrate in 10 ml of methanol and then a solution of 1 g of (Ia) in 10 ml of methanol was also added. The methanol was evaporated, the residue diluted with water and the precipitate collected by filtration, washed with water, methanol and ether and recrystallized from 100 ml of alcohol. We obtained 0.39 g (50%) of dark red prisms with a green lustre and m. p. 175°. In chloroform they had λ_{max} 515 and 335 mμ (lg ε 4.43 and 4.10), in alcohol λ_{max} 510, 336 and 326 mμ (lg ε 4.20, 4.39 and 4.05) and in alcohol in the presence of sulfuric acid λ_{max} 385 and 242 mμ (lg ε 4.03 and 4.39).

Found %: S 11.50, 11.69. $C_{18}H_{15}NS$. Calculated %: S 11.56.

N-Methyl-2-(α-ethyleneiminostyryl)-quinolinium perchlorate (V). To a solution of 0.2 g of (Ia) in 2 ml of methanol was added 0.1 ml of ethyleneimine and then a solution of 0.1 g of sodium perchlorate in methanol. The precipitate was washed with methanol and ether. The yield was 0.17 g (78%). The preparation crystallized from alcohol as yellow needles with m. p. 190-191°; in alcohol it had λ_{max} 410 mμ (lg ε 4.32).

Found %: N 7.48, 7.46. $C_{20}H_{14}O_4N_2Cl$. Calculated %: N 7.24.

N- Methyl-2-(α-piperidylstyryl)-quinolinium iodide (VI). To a solution of 0.2 g of (Ia) in 3 ml of methanol was added 0.1 ml of piperidine. The dark yellow solution was concentrated on a water bath and the dye precipitated with ether. The precipitate was dissolved in 20 ml of boiling water and potassium iodide added. When the solution was cooled, it deposited the iodide of the dye as yellow leaflets. Drying in vacuum at 110° yielded 0.17 g (65%) of the iodide with m. p. 194°. In an alcohol solution it had λ_{max} 448 mμ (lg ε 4.49).

Found %: I 27.80, 27.76. $C_{23}H_{25}N_2I$. Calculated %: I 27.81.

N-Methyl-2-(α-anilinostyryl)-quinolinium methosulfate (VII). To a solution of 1 g of (Ia) in 3 ml of methanol was added 0.26 g of aniline and then 20 ml of ether. An oil precipitated and this crystallized after being stirred with two drops of water. The substance was recrystallized from 30 ml of water. The brown prisms contained water of crystallization. After being dried in vacuum at 110°, the product had m. p. 159° and the yield was 0.68 g (54%). In an alcohol solution, the substance had λ_{max} 457 mμ (lg ε 4.51).

Found %: N 6.13, 6.18. $C_{25}H_{24}O_4N_2S$. Calculated %: N 6.24.

2-[α-Phenyl-β-(1'-methyldihydroquinolinylidene)-ethylidene]-acetoacetic ester (VIII) was obtained by mixing 0.2 g of (Ia) and 0.2 g of acetoacetic ester in 1 ml of methanol with 0.2 ml of triethylamine. The precipitate formed was washed on the filter with methanol and ether. After recrystallization from 5 ml of benzene, the precipitate yielded 0.10 g (48%) of product; in alcohol it had λ_{max} 540 mμ (lg ε 4.12), and in chloroform, λ_{max} 516 mμ and the m. p. was 184° (with decomp.).

Found %: N 3.88, 4.03. $C_{24}H_{23}O_3N$. Calculated %: N 3.75.

2-[α-Phenyl-β(1'-methyldihydroquinolinylidene)-ethylidene]-benzoylacetone (IX). The preparation was obtained similarly to the previous one from 0.2 g (Ia) and 0.2 g of benzoylacetone. When the product had been recrystallized from benzene, the yield was 0.17 g (74%) and the m. p. 165°. In alcohol it had λ_{max} 544 mμ (lg ε 4.28).

Found %: N 3.49, 3.58. $C_{28}H_{23}O_2N$. Calculated %: N 3.46.

1,1'-Dimethyl-10-phenyl-2,2'-quinocarbocyanine iodide* (X). 0.13 g of (Ib) and 0.18 g of the iodomethylate of quinaldine were dissolved in 5 ml of alcohol and 0.03 g of triethylamine added to the solution. The precipitated dye was washed on the filter with alcohol and ether. The golden green prisms had m. p. 239-240° (with decomp.). The yield was 0.12 g (73%); in alcohol it had λ_{max} 648 and 366 mμ (lg ε 4.84 and 4.24). Literature data for this dye [10]: in methyl alcohol, λ_{max} 642 mμ (lg ε 4.78).

Found %: I 23.88, 23.85. $C_{29}H_{25}N_2I$. Calculated %: I 24.02.

1,3'-Dimethyl-10-phenyl-2-quinothiacarbocyanine perchlorate (XI). The dye was obtained similarly to the previous one from 0.2 g of (Ia) and 0.17 g of the methyl methosulfate of 2-methylbenzthiazole. When the product had been recrystallized from 100 ml of alcohol, the yield was 0.13 g (46%). The prisms with a bronze lustre had m. p. 259°; in alcohol they had λ_{max} 603 and 366 mμ (lg ε 5.00 and 4.15).

Found %: Cl 6.66, 6.67. $C_{27}H_{23}O_4N_2Cl$. Calculated %: Cl 6. 99.

1,3'-Diethyl-10-phenyl-2-quino-6',7'-benzothiacarbocyanine iodide (XII) was obtained similarly to the previous product from 0.2 g of the ethyl ethosulfate of 2-phenylacetylenylquinoline and 0.22 g of the ethyl ethosulfate of 2-methylnaphthothiazole. The dye was precipitated from alcohol solution with sodium iodide. The yield was 0.29 g (84%). After recrystallization from alcohol, the product formed prisms with a greenish lustre. The m. p. was 233° (with decomp.); in alcohol the product had λ_{max} 618 and 370 mμ (lg ε 495 and 407)

Found %: I 21.30, 21.12. $C_{33}H_{29}N_2SI$. Calculated %: I 20.72.

1,3'-Diethyl-5'-methoxy-10-phenyl-2-quinoselenacarbocyanine perchlorate (XIII). The dye was obtained similarly to the previous one from 0.186 g of the ethyl perchlorate of 2-phenylacetylenylquinoline and 0.25 g of the ethyl p-toluenesulfonate of 2-methyl-5-methoxybenzeselenazole. When the product had been recrystallized from 50 ml of alcohol, the yield was 0.111 g (35%). The small tablets with a green lustre had m. p. 230° (with decomp.) and in alcohol, λ_{max} 616 mμ (lg ε 4.97)

Found %: N 4.65, 4.54. $C_{30}H_{29}O_5N_2SeCl$. Calculated %: N 4.58.

1,1',3',3'-Tetramethyl-10-phenyl-2-quinoindocarbocyanine perchlorate (XIV) was obtained from 0.2 g of (Ia) and 0.19 g of the iodomethylate of 3,3-dimethylindolenine and precipitated with sodium perchlorate. When the product had been recrystallized from 15 ml of alcohol, the yield was 0.13 g (45%) of fine leaflets

* The chloride, bromide and picrate of this dye were obtained by Rosenhauer [11] by another method.

with a green lustre. The m. p. was 233-234°; in alcohol, the product had λ_{max} 596 and 375 mμ (lg ε 4.60 and 4.20).

Found %: N 5.51, 5.57. $C_{30}H_{29}O_4N_2Cl$. Calculated %: N 5.42.

3-Methyl-5-[α-phenyl-β-(1'-methyldihydroquinolinylindene-2')-ethylidene]-rhodanine (XV). To a mixture of 1 g of (Ia) and 0.5 g of 3-methylrhodanine in 20 ml of methanol was added 0.28 g of triethylamine. After 30 minutes, the liquid was sucked off and the dye washed with methanol and ether. The yield was 0.96 g (86%). After recrystallization from chloroform, the product formed leaflets with a green lustre. The m. p. was 285°; in alcohol, the product had λ_{max} 598 mμ; in chloroform, λ_{max} 600, 575 and 430 mμ (lg ε 4.72, 4.75 and 3.63).

Found %: N 7.01, 7.13. $C_{22}H_{18}ON_2S_2$. Calculated %: N 7.18.

The same dye was obtained from N-methyl-2-thiobenzoylmethenedihydroquinoline (IV), methyl p-toluenesulfonate and 3-methylrhodanine in 45% yield; the m. p. was 282°.

1-Phenyl-3-methyl-4-[α-phenyl-β-(1'-methyldihydroquinolinylindene-2')-ethylidene]-pyrazolone-5 (XVI) was obtained from 0.2 g of (Ia) and 0.11 g of phenylmethylpyrazolone by the same method as for dye (XV). The yield was 0.103 g (44%) and the product crystallized from alcohol as prisms with a golden lustre. The m. p. was 250° (with decomp.); in alcohol, the product had λ_{max} 545 and 408 mμ (lg ε 4.51 and 3.96), in chloroform, λ_{max} 561 and 455 mμ (lg ε 4.54 and 4.04).

Found %: N 10.24, 10.33. $C_{28}H_{23}ON_3$. Calculated %: N 10.07.

SUMMARY

It was found that quaternary salts of 2-phenylacetylenylquinoline readily added sodium hydrosulfide, amines and compounds with active methyl and methylene groups. It was shown that heterocyclic derivatives of an acetylene of the 2-phenylacetylenylquinoline type could be used as intermediates in the synthesis of cyanine dyes substituted in the chain.

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INVESTIGATION OF AQUEOUS SOLUTIONS OF SUCCINIC ACID BY THE RAMAN SPECTRUM

A. A. Glagoleva and A. A. Ferkhmin
L. M. Sechenov Institute of Evolutionary Physiology

In previous work, we investigated the behavior of acetic acid in aqueous solutions of various concentrations [1].

It is known that under certain conditions succinic acid may be formed from acetic acid through the intermediate formation of radicals ($-CH_2COOH$) [2, 3].

As is known, in living organisms succinic acid is connected with cell respiration, for example in liver cells; it participates in fermentative processes in respiration and intensifies it [2, 4].

We considered it appropriate, after a careful study of acetic acid, to begin an investigation of aqueous solutions of succinic acid by the Raman spectrum. The Raman spectrum of succinic acid in water is given in only one article [5] and without any indication of the concentration. The frequency region pertaining to the succinic acid radical was not examined in this work. Data are available for succinic acid [6] and its anhydride [7, 8] in the crystalline state.

Unfortunately, the solubility of succinic acid in water is very limited. We were unable to obtain a solution of more than 6% concentration at the temperature at which we worked (about 9°), since supersaturation occurred and crystals were deposited by the solution. We investigated the following solution concentrations (in weight %): 5.99, 5.90, 5.80, 5.70, 5.60, 5.50, 5.30, 5.20, 4.90, 4.80, 4.73, and 4.30.

The conditions for plotting the Raman spectra were the same as in the case of acetic acid [1]. Microphotometric curves were obtained with an MF-2 microphotometer and the measurements were made on an IZA-2 horizontal comparator.

Figure 1 shows microphotometric curves for solutions of 5.93, 4.73 and 4.30% concentration and for water in the frequency range 2625-3750 cm^{-1}.

For the CH_2 group of succinic acid, we obtained the following frequencies in the order of decreasing intensity; 2943 (most intense), 2987, 3011, 2888 cm^{-1} and the two frequencies 2970 and 2910 cm^{-1}, which are doubtful. In Table 1, we compare these frequencies with the corresponding frequencies of acetic acid (our data, obtained as average values from the frequencies at all the concentrations we measured).

For this region of the spectrum there is no data in the literature on the succinic acid radical; there is only a report of the frequencies 2953 and 2992 cm^{-1} for succinic anhydride [7, 8].

It is reported in the literature that with an increase in the length of the carbon chain, the frequency of the C–C bond decreases [7, 10]. From a large number of measurements of the spectra of solutions at various concentrations, we obtained the frequency 845 cm^{-1}. Apparently, this bond is complex (Fig. 2). We ascribe the frequency of 930 cm^{-1} to the light source.

We ascribe two frequencies, 1703 (more intense) and 1735 cm^{-1} to the C = O bond. Microphotometric curves are given for a concentrated solution of succinic acid (5.93%), the most dilute solution of it (4.30%) and water (Fig. 3).

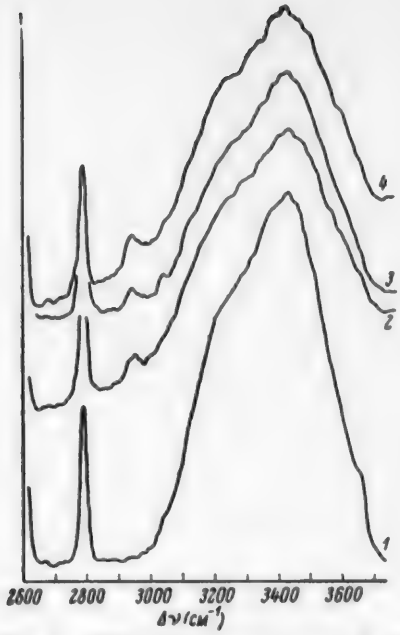


Fig. 1. Microphotometric curves of the Raman spectrum of aqueous solutions of succinic acid and water in the frequency region 2625-3750 cm^{-1}. 1) Water, 2) 4.30% solution, 3) 4.73% solution, 4) 5.93% solution.

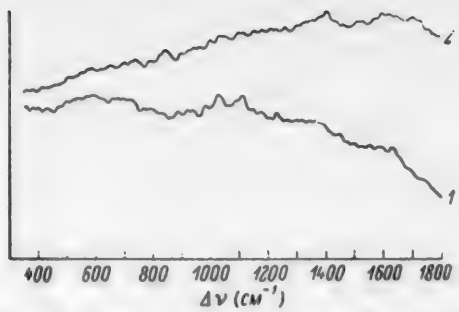


Fig. 2. Microphotometric curves of Raman spectra for an aqueous solution of succinic acid and water in the frecuency region 1350-1800 cm^{-1}. 1) Water, 2) 5.93% solution.

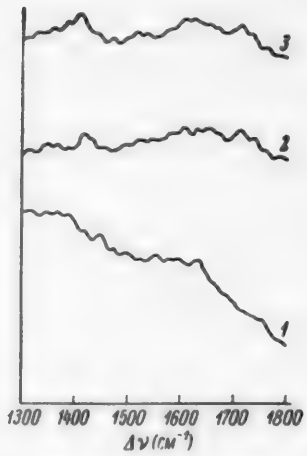
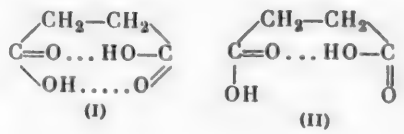


Fig. 3. Microphotometric curves of Raman spectra for aqueous solutions of succinic acid and water in the frequency region 1300-1800 cm^{-1}. 1) Water, 2) 4.30% solution, 3) 5.93% solution.

At first glance, the relatively high intensity of the band at 1703 cm^{-1} of the C = O group at 4.30% concentration seems strange in comparison with its intensity for a 5.93% solution. It seemed possible to us to explain this in the following way: according to the physicochemical data of one of the authors of this article [11], at a concentration of 5.93% almost all the succinic acid molecules have the closed structure (I). This structure has two intramolecular hydrogen bonds with different dissociation constants ($0.63 \cdot 10^{-4}$ and $3.3 \cdot 10^{-6}$) [12]. With a decrease in the concentration, the bond with the greatest dissociation constant is ruptured and the number of molecules of type (II) is increased.



Apparently, the band at 1703 cm^{-1} (and perhaps that at 1735 cm^{-1}) pertains to the open C = O bond. Hence, the relative increase in the intensity of these bands in a solution at a concentration of 4.30% is understandable.

Figure 3 clearly shows a band at 1408 cm^{-1}, which, in our opinion, corresponds to the C–O or C–OH group. Apparently, it has a complex structure.

Table 2 gives a comparison of our data for the frequency region 800-1800 cm^{-1} with data available in the literature.

TABLE 1

Acid	Frequencies of CH_2 groups (cm^{-1})					
Succinic	2888	2910	2943	2970	2987	3011
Acetic	2880		2944		2990	3023

TABLE 2

Object of examination	Frequency of groups (cm^{-1})					Literature reference
	C=O		C—O or C—OH		C—C	
Crystalline succinic acid	—	—	—	1420	927	[6]
Aqueous solution of succinic acid of unknown concentration	1702	—	1409	—	837 935	[5]
Aqueous solutions of succinic acid (concentration of 5.99 to 4.30%)	1703	1735	1408	1424 (?)	845	Our data
Succinic anhydride	1678	—	1413	—	813	[7]
The same	1703	1753	1400	1431	854	[8]

SUMMARY

1. The Raman spectra of succinic acid in aqueous solutions at various concentrations are given.

2. According to our hypothesis, at a concentration of 5.93% the solution contains a certain amount of succinic acid molecules with one broken intramolecular hydrogen bond.

3. With a decrease in the succinic acid concentration, the amount of molecules with one broken intramolecular hydrogen bond in the solution increases. The amount of such molecules becomes great, even at an acid concentration of 4.30%.

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REFLECTION OF PICRATE FORMATION ON CURVES OF ULTRAVIOLET ABSORPTION SPECTRA

N. Z. Rudenko

Stalin State Medical Institute

In the investigation of intermolecular interaction by physicochemical analysis methods, one sometimes encounters the fact that such well-proven methods as the determination of melting point, viscosity, electroconductivity, etc., can not be used. This usually arises in cases where the components under investigation decompose before the melting point or when the components melt without decomposition, but mixtures of them decompose on melting and, finally, when the melting point of one component is close to the boiling point or even above the boiling point of the other.

In some of our work on the interaction of symmetrical diphenylurea with organic acids, due to the reasons presented above, we were unable to use the physicochemical analysis methods listed. We were able to solve the problem of the intermolecular reaction by means of absorption spectroscopy on aqueous solutions [1].

It should be noted that in the literature, the problem of the reflection of intermolecular reaction on absorption spectrum curves has largely been examined as a hindrance in analysis and has been used very little for the elucidation of complex formation. This refers particularly to the ultraviolet part of the spectrum [2-4].

The well-developed method of determining complex formation, based on the change in optical density in relation to the relative concentrations of the reacting components [5, 6], does not always give positive results. In connection with this, the analysis of absorption curves of mixtures of two components seemed particularly interesting for conclusions on the intermolecular interaction between these components. In the presence of chemical interaction between the components, the absorption curves calculated on the basis of Beer s law (additive curves) need not agree with the curves obtained experimentally.

This work was aimed at determining whether intermolecular reaction would be reflected in the absorption curves and if so, to what extent the form of these curves would change in comparison with the additive curve, whether the number and position of the "salient points" would change and to what extent and also in what region would be the maximum discrepancy between the experimental and the additive curve. We also proposed to determine to what extent the stability of the molecular compound, replacement of the solvent and a change in the concentration of the components would affect the magnitude of the discrepancy between the actual and the additive absorption curves.

To solve these problems, we investigated the reflection of picrate formation in the ultraviolet absorption curves. Picrates were chosen for the reason that they are in general extremely stable molecular compounds of quite definite composition; in addition, they may be readily obtained, isolated and purified. Since most of the substances with which we were proposing to work were quite transparent in the visible region of the spectrum, we only investigated the ultraviolet part of the spectrum.

Despite the abundance of picrates, the choice of components for the investigation required some preliminary work with the given solvents, since it was limited by a series of conditions. It was necessary that all the components were sufficiently soluble in the solvents used; in addition, all the starting components and the picrates themselves had to obey Beer's law, even if at great dilution; finally, it was desirable that the picrates differed from each other in stability.

The picrates of pyridine, p-toluidine and urea were chosen for the work. The relative stabilities of these picrates may to some extent be characterized by the ratio of the melting point of the picrate to the arithmetic mean of the melting points of the separate components. Pyridine picrate is most stable (ratio equals 4.12), then p-toluidine picrate (2.03) and finally, urea picrate (1.18).

The solvents were chosen so that their dielectric permeabilities were as different as possible. The solvents used were water (ϵ = 81), ethyl alcohol (ϵ = 25.8) and carbon tetrachloride (ϵ = 2.23) [7].

In the present work we present the results of investigating the ultraviolet absorption spectra of picric acid, pyridine, p-toluidine, urea, mixtures of picric acid with pyridine, p-toluidine and urea and also pyridine, p-toluidine and urea picrates in the three solvenrs at various concentrations.

The absorption spectra were measured on an SF-4 spectrophotometer and the experimental procedure did not differ from the one we described previously [1]. The choice of concentration was determined by the optical density, which as far as possible was in the range from 0.1 to 1.

The concentrations of the working solutions used for the spectroscopic measurements were as follows: $2.5 \cdot 10^{-5}$ and $5 \cdot 10^{-5}$ M in water and alcohol for picric acid, p-toluidine, pyridine, urea, and the corresponding picrates and $5 \cdot 10^{-5}$ M in carbon tetrachloride for p-toluidine and pyridine. Picric acid and urea are very difficultly soluble in carbon tetrachloride; therefore, the working solutions of picric acid in carbon tetrachloride were prepared by dilution of 2 ml of a solution saturated at 18.6° to 100 ml and the solutions of urea in carbon tetrachloride by dilution of 50 ml of a solution saturated at 20.2° to 100 ml. The absorption curves of these solutions were in the same region of the spectrum as the curves for $5 \cdot 10^{-5}$ M alcohol and aqueous solutions of these components (Fig. 1).

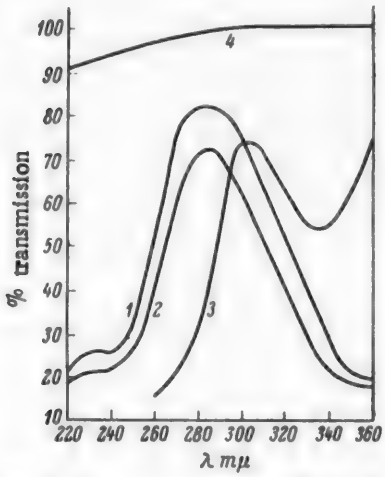

Fig. 1. Transmission curves of $5 \cdot 10^{-5}$ M solutions of picric acid and urea. 1) $C_6H_2(NO_2)_3OH$ in alcohol, 2) $C_6H_2(NO_2)_3OH$ in water, 3) $C_6H_2(NO_2)_3OH$ in carbon tetrachloride, 4) $CO(NH_2)_2$ in alcohol, water and carbon tetrachloride.

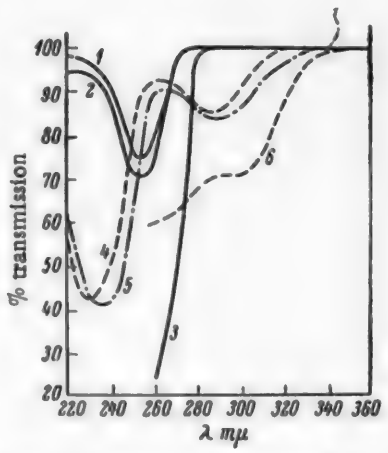

Fig. 2. Transmission curves of $5 \cdot 10^{-5}$ M solutions of pyridine and p-toluidine. 1) C_5H_5N in alcohol, 2) C_5H_5N in water, 3) C_5H_5N in carbon tetrachloride, 4) $p\text{-}CH_3C_6H_4NH_2$ in water, 6) $p\text{-}CH_3C_6H_4NH_2$ in carbon tetrachloride.

Solutions of mixtures were prepared by mixing equal volumes of solutions of the starting components, whose concentrations were twice those of the working solutions.

The water used was triply distilled. After being dried over fired copper sulfate, the ethyl alcohol was also distilled three times. The anhydrous carbon tetrachloride used was distilled twice with collection of the fraction boiling in the range 76.8-76.9°. The p-toluidine was purified by conversion into acettoluidine with acetic anhydride and this was then hydrolyzed and the p-toluidine recrystallized twice from alcohol (m. p. 44.8°). Anhydrous pyridine was purified by two distillations and the fraction with b. p. 115.9° collected. Picric

acid and urea were purified by the method described previously and had the constants presented in [8]. Comparison cells were filled with the appropriate solvent. The cell thickness was 10 mm.

To check that the solutions of the separate components and the picrates obeyed Beer's law and that there were no apparent deviations from this law, we investigated the dependence of light absorption on concentration in appropriate solvents. For picric acid, pyridine, p-toluidine and their picrates and also for urea picrate in water and alcohol, we examined solutions in the concentration range from $5 \cdot 10^{-6}$ to $8 \cdot 10^{-5}$ M and in carbon tetrachloride, from 0.1 c to 1.5 c (c is the working concentration). The extinction coefficients calculated from the data obtained were constant at a given wavelength, regardless of the concentration.

The investigation was carried out at constant temperature in the wavelength region from 220 to 360 mμ in water and alcohol and from 260 to 360 mμ in carbon tetrachloride, since carbon tetrachloride is opaque up to 260 mμ. The curves did not change their form when the solutions were stored for seven days.

It is known that the same substance can have different absorption curves in different solvents [2, 3]. Investigation showed that our components also had different forms of absorption curves in different solvents (Figs. 1 and 2). For all three components, replacement of water and alcohol by carbon tetrachloride led to a shift in the absorption curves towards longer wavelengths. To a lesser extent, the replacement of one polar solvent by another had an effect; thus, the transmission bands of picric acid in water (Fig. 1) were shifted by 4 mμ with respect to the same bands in alcohol, while in the case of carbon tetrachloride, this shift was 25 mμ. This discrepancy of the curves is possible when the component reacts to some extent with the solvent [9-11], as also cannot be excluded for our polar solvents. However, detailed investigations of the effect of solvent on the form

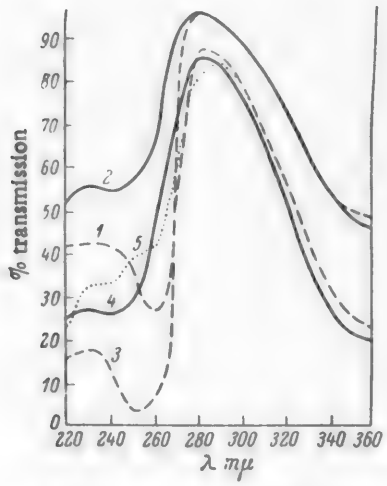

Fig. 3. Transmission curves of alcohol solutions. 1) $2.5 \cdot 10^{-5}$ M mixture of $C_5H_5N + C_6H_2(NO_2)_3OH$, 2) additive curve of the same mixture, 3) $5 \cdot 10^{-5}$ M mixture of $C_5H_5N + C_6H_2(NO_2)_3OH$, 4) additive curve of the same mixture, 5) $5 \cdot 10^{-5}$ M picrate $C_5H_5N \cdot C_6H_2(NO_2)_3OH$.

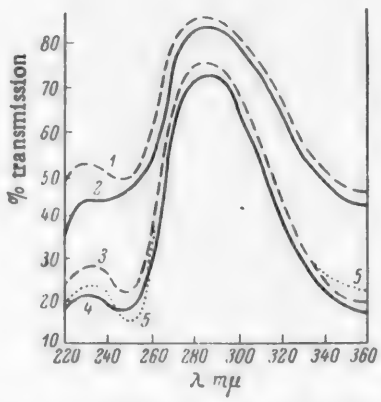

Fig. 4. Transmission curves of aqueous solutions. 1) $2.5 \cdot 10^{-5}$M mixture of $C_5H_5N + C_6H_2(NO_2)_3OH$, 2) additive curve of the same mixture, 3) $5 \cdot 10^{-5}$ mixture of $C_5H_5N + C_6H_2(NO_2)_3OH$, 4) additive curve of the same mixture, 5) $5 \cdot 10^{-5}$ M picrate $C_5H_5N \cdot C_6H_2(NO_2)_3OH$.

of the absorption curve, carried out in the visible part of the spectrum, showed that shifts in the curves were also observed in the absence of interaction between solvent and solute [12].

A study of the systems we chose showed that the formation of picrates affected the absorption curves regardless of the solvent used.

In the pyridine–picric acid systems there was a particularly great discrepancy between the additive and the experimentally obtained transmission curves in alcohol solutions (Fig. 3). Here the discrepancy in the region of

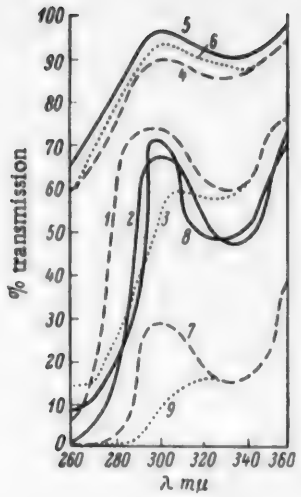

Fig. 5. Transmission curves of carbon tetrachloride solutions. 1) $5 \cdot 10^{-5}$ M mixture of $C_5H_5N + C_6H_2(NO_2)_3OH$; 2) additive curve of the same mixture; 3) $5 \cdot 10^{-5}$ M picrate of $C_5H_5N \times$ $\times C_6H_2(NO_2)_3OH$; 4) $5 \cdot 10^{-5}$ M mixture of $CO(NH_2)_2 + C_6H_2(NO_2)_3OH$, 5) additive curve of the same mixture, 6) $5 \cdot 10^{-5}$ M picrate of $CO(NH_2)_2 \cdot C_6H_2(NO_2)_3OH$, 7) $5 \cdot 10^{-5}$ M mixture of $p\text{-}CH_3C_6H_4NH_2 +$ $+ C_6H_2(NO_2)_3OH$, 8) additive curve of the same mixture, 9) $5 \cdot 10^{-5}$ picrate $p\text{-}CH_3C_6H_4NH_2 \cdot C_2H_6(NO_2)_3OH$.

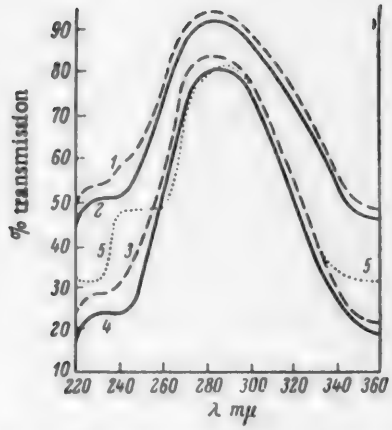

Fig. 6. Transmission curves of alcohol solutions. 1) $2.5 \cdot 10^{-5}$ mixture of $CO(NH_2)_2 + C_6H_2(NO_2)_3OH$, 2) additive curve of the same mixture, 3) $5 \cdot 10^{-5}$ mixture of $CO(NH_2)_2 + C_6H_4(NO_2)_3OH$, 4) additive curve of the same mixture, 5) $5 \cdot 10^{-5}$ picrate $CO(NH_2) \cdot$ $\cdot C_6H_4(NO_2)_3OH$.

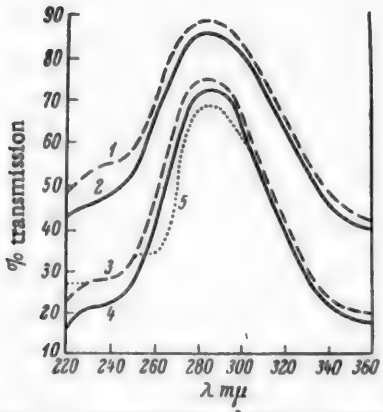

Fig. 7. Transmission curves of aqueous solutions. 1) $2.5 \cdot 10^{-5}$ M mixture of $CO(NH_2)_2 + C_6H_2(NO_2)_3OH$, 2) additive curve of the same mixture, 3) $5 \cdot 10^{-5}$ M mixture of $CO(NH_2)_2 + C_6H_2(NO_2)_3OH$, 4) additive curve of the same mixture, 5) $5 \cdot 10^{-5}$ M picrate $CO(NH_2) \cdot C_6H_2(NO_2)_3OH$.

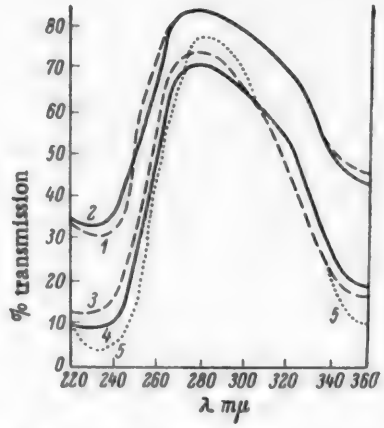

Fig. 8. Transmission curves of alcohol solutions. 1) $2.5 \cdot 10^{-5}$ M mixture of $p\text{-}CH_3C_6H_4NH_2 + C_6H_2(NO_2)_3OH$, 2) additive curve of the same mixture, 3) $5 \cdot 10^{-5}$ M mixture of $p\text{-}CH_3C_6H_4NH_2 + C_6H_4(NO_2)_2OH$, 4) additive curve of the same mixture, 5) $5 \cdot$ $\cdot 10^{-5}$ M picrate $p\text{-}CH_3C_6H_4NH_2 \cdot C_6H_2(NO_2)_3OH$.

the absorption band (250-260 mμ) reached 40%. The deviation for aqueous solutions and solutions and solutions in carbon tetrachloride (Figs. 4 and 5) was somewhat less (6-8%). The figures show that the greatest discrepancy is observed in the shorter wavelength part of the spectrum (from 220 to 260-280 mμ). In carbon tetrachloride solutions, however, the absorption is approximately the same for all wavelength regions. The curves actually obtained (Figs. 3 and 4) show more pronounced absorption maxima and minima than the additive ones: for alcohol solutions, the minima are even displaced relative to each other (Fig. 3). It is interesting that, depending on the solvent, the actual curves lie either above (water and carbon tetrachloride) the additive curve or below it in the shortwave part and above it in the longwave part of the spectrum (alcohol).

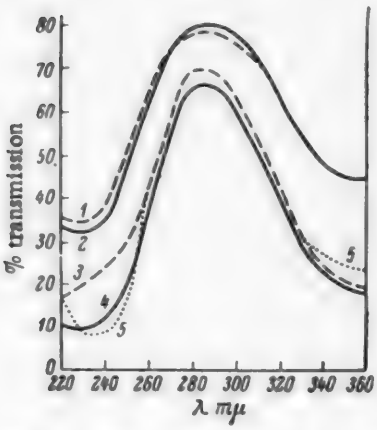

Fig. 9. Transmission curves of aqueous solutions. 1) $2.5 \cdot 10^{-5}$ M mixture of $p\text{-}CH_3C_6H_4NH_2 + C_6H_2(NO_2)_3OH$, 2) additive curve of the same mixture, 3) $5 \cdot 10^{-5}$ M mixture of $p\text{-}CH_3C_6H_4NH_2 + C_6H_2(NO_2)_3OH$, 4) additive curve of the same mixture, 5) $5 \cdot 10^{-5}$ M picrate $p\text{-}CH_3C_6H_4NH_2 \cdot C_6H_2(NO_2)_3OH$.

In the urea – picric acid systems (Figs. 5-7), the discrepancy between the additive and experimental curves was somewhat less than in the case of the previous systems, though here also it was maximal in the shortwave region, reaching 9% at 240 mμ. For carbon tetrachloride, a discrepancy of the order of 6-8% is observed at all wavelengths. In systems with urea, the actual curves lie above the addition ones with the exception of solutions in carbon tetrachloride.

In the p-toluidine – picric acid systems (Figs. 5, 8 and 9) approximately the same rules are observed as for previous systems. Here the discrepancy between the additive and experimental absorption curves in carbon tetrachloride is particularly great and over almost the whole of the wavelength region investigated it is 30-40%. In contrast to the first system, the position of the "salient points" for the two forms of the curves remains unchanged. The figures show that with an increase in the concentration of the components, the discrepancy between the additive and the actual curves increases to a very small extent (maximal in carbon tetrachloride solution).

Our hypothesis that with an increase in the stability of the picrate there would be an increase in the discrepancy between the actual and the additive curves was only partially confirmed, namely for the most stable picrate, that of pyridine.

It might be surmised that the experimental absorption curves of mixtures, which substantially reflect picrate formation, would agree completely with the absorption curves of the picrates in the same solvent. To test this hypothesis, we examined the absorption curves of the corresponding picrates. A comparison of these curves with corresponding absorption curves of mixtures and picrates do not coincide with each other regardless of the solvents used. The greatest discrepancy between these curves is observed for solutions in carbon tetrachloride, then in alcohol and finally in water.

SUMMARY

1. An investigation was made of the ultraviolet absorption curves of picric acid, pyridine, p-toluidine, urea, equimolecular mixtures of picric acid with pyridine, p-toluidine and urea and also the picrates of pyridine, p-toluidine and urea at various concentrations in three solvents, namely water, ethyl alcohol and carbon tetrachloride.

2. It was shown that the formation of picrates leads to a discrepancy between the experimental absorption curves and the curves calculated on the basis of Beer's law, but that the number and position of the "salient points" does not change as a rule.

3. It was found that the greatest discrepancy between the actual and additive curves was observed in the shortwave part of the spectrum; it was greater, the lower the polarity of the solvent.

4. It was established that the spectral curves of picrates and corresponding mixtures in the same solvent did not agree with each other.

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INVESTIGATION OF THE ALKALOIDS OF UNGERNIA SEVERTZOVII

STRUCTURE OF UNGERINE

S. Yu. Yunusov and Kh. A. Abduazimov

Institute of the Chemistry of Vegetable Materials, Academy of Sciences
Uzbek, SSR

In a previous article [1], we reported an investigation on alkaloids of the species ungernia. Then we isolated from the bulb of u. Severizovii (Rgl.) B. Fedsch., in addition to the known lycorine and tazettine, two new alkaloids:

(I) – ungerine $C_{17}H_{18}O_2(N)(CH_2O_2)(OCH_3)(=)$ and

(II) – ungeridine $C_{18}H_{19}(N)(CH_2O_2)(OCH_3)(OH)(=)$.

To elucidate the structure of the basic substance of these new alkaloids, we distilled ungerine (I) with zinc dust. It was possible to isolate phenanthridine from the reaction products.

We obtained further data on the structure of ungerine (I) by subjecting it to a Hofmann degradation. The action of silver hydroxide on the iodomethylate of ungerine (III) yielded optically inactive crystalline des-N-methylungerine (IV) with the composition $C_{19}H_{21}O_4N$ and which did not contain a methoxy group. This substance had a weakly basic character, was difficultly soluble in organic solvents and gave crystalline salts, namely the hydrochloride, hydrobromide and nitrate.

The disappearance of the methoxyl group from the molecule of (III) indicated that during the Hofmann degradation, the methoxyl group was eliminated as methyl alcohol. This formed a new aromatic ring, where a tetrahydrobenzene ring had been. In order to confirm the aromatization of tetrahydrobenzene ring B in the molecule of ungerine (I), des-N-methylungerine (IV) was oxidized with potassium permanganate. As a result, we obtained benzoic acid, which was not formed by ungerine itself.

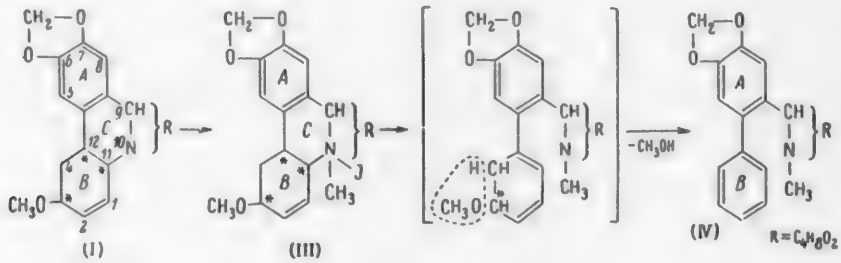
The iodomethylate (III) did not undergo a Hofmann or an Emde degradation. To obtain a nitrogen-free product, we carried out a Hofmann degradation on the iodomethylate of dihydroungerine. On degradation, the latter gave des-N-methyldihydroungerine as an oily mass, which gave a crystalline nitrate and iodomethylate.

The iodomethylate of des-N-methyldihydroungerine could not be subjected to further Hofmann degradation. Des-N-methyldihydroungerine contained a methoxyl group. This indicated that in the absence of the double bond, the aromatization of benzene ring B in the ungerine molecule did not occur during Hofmann degradation.

Oxidation of ungerine (I) with potassium permanganate yielded hydrastic acid. Consequently, the methylenedihydroxy group was in an aromatic ring. In the molecule of ungerine (I), the aromatic ring A was more stable to oxidation and the partially hydrogenated rings B and C were oxidized.

On the basis of the data presented above, we proposed for ungerine the partial structural formula (I). The double bond in formula (I) could not be between carbon atoms 1-11 or 11-12 because in the Hofmann degradation with the appearance of a new double bond, there would be two degradation with the appearance of a new double bond, there would be two double bonds next to each other. Then, we would not obtain a benzene ring or, correspondingly, benzoic acid in the oxidation of des-N-methylungerine (IV). The double bond in formula (I) may be between carbon atoms 1-2, 2-3, 3-4 or 4-12. We consider it improbable that the methoxyl

group is at atoms 1, 11 or 12 (in analogy with alkaloids of the phenanthridine series [2]). Then in formula (I) there remains the possibility of the methoxyl group being at carbon atom 2, 3 or 4. It is most probable that in formula (I) the double bond is between carbon atoms 1-2 and the methoxyl group in position 3. The mechanism of aromatization of ring B and the disappearance of the asymmetric carbon atoms during aromatization may be explained in the following way.



In the first stage of the Hofmann degradation of ungerine, on the elimination of one hydrogen atom from carbon atom 12 a new double bond appears between atoms 11-12 with rupture of the bond between carbon atom 11 and the nitrogen atom. Hence, the asymmetric centers at carbon atoms 11 and 12 disappear. The appearance of a second double bond in ring B increases the tendency towards full aromatization of this ring. Therefore the third double bond in ring B is produced very readily as a result of elimination of the methoxyl group at atom 3 and one hydrogen from carbon atom 4. As the tetrahydrobenzene ring B becomes aromatic, all three carbons lose their asymmetry and optically inactive des-N-methylungerine is obtained.

In formula (I), the character of the residue $C_4H_8O_2$ remains unclear. This residue cannot be attached to ring A or to ring B, since on oxidation of ungerine (I) we obtained hydrastic acid and on oxidation of compound (IV), benzoic acid. Had the residue $C_4H_8O_2$ been attached to ring A or B, oxidation could not have yielded these acids, but would have given di- or tribasic acids. This residue may be attached to the nitrogen atom and to carbon atom 9, forming a new ring. It could also be in the form of an open chain at the nitrogen or at carbon atom 9.

EXPERIMENTAL

Distillation of ungerine with zinc dust. 5 g of ungerine were mixed with 60 g of zinc dust and 1 g of finely divided asbestos and placed in a refractory tube. With a rapid flow of hydrogen through it, the tube was heated to a dull red heat. The distillable part was collected in 5% sulfuric acid. The sulfuric acid solution was made alkaline and the distillation products extracted with ether. Concentration of the ether solution yielded 0.3 g of a tarry mass, which was dissolved in hydrochloric acid. When an aqueous solution of mercuric chloride was added to the hydrochloric acid solution obtained, a white precipitate with m. p. 171-172° formed immediately. When the product was recrystallized from 5% hydrochloric acid, the melting point was raised to 189-190°. A mixed melting point of this substance with the binary mercury salt of phenanthridine, obtained from tazettine, was not depressed.

Oxidation of ungerine. 1 g of ungerine was dissolved in 15 ml of 2% sulfuric acid and the solution neutralized until turbidity appeared. To the neutral solution was added a 1% solution of potassium permanganate (525 ml). The solution was left until it was decolorized completely. Then the precipitated mixture of manganese dioxide and potassium salts was collected by filtration. The precipitate was washed several times with a 3% solution of potassium hydroxide. The aqueous mother solution was acidified with concentrated hydrochloric acid and extracted with ether. Removal of the ether left 0.25 g of a brownish yellow tarry mass, which was dissolved in an alcohol solution of methylamine. This solution was concentrated, heated for 15 minutes at 180-190° and then distilled at 155-160° (5 mm). This yielded a white crystalline substance with m. p. 226-227°, undepressed by admixture with the methylamide of hydrastic acid obtained from tazettine.

Found %: N 6.64. $C_{10}H_7O_4N$. Calculated %: N 6.82.

Des-N-methylungerine (IV). To 20 g of the iodomethylate of ungerine with m. p. 265-266°, dissolved in 100 ml of methanol, was added freshly precipitated silver oxide, obtained from 0.7 g of silver nitrate. The mixture was shaken for 2 hours until the solution no longer gave a positive reaction for halide. The reaction mixture was heated on a water bath under reflux for 30 minutes. The evolution of trimethylamine was not observed. The precipitate of silver iodide was removed by filtration and the alcohol evaporated. The oily residue formed a powder on drying in vacuum. The yield was 1.35 g. After recrystallization from methanol, the des-N-methylungerine melted at 155-156°; it was optically inactive.

Found %: C 69.31; H 6.09; N 4.38; NCH_3 6.31. $C_{19}H_{21}O_4N$. Calculated %: C 69.7; H 6.46; N 4.27; NCH_3 4.59.

The absence of a methoxyl group was established by analysis.

The hydrochloride precipitated in the form of needles (m. p. 276-277°) when alcohol solutions of des-N-methylungerine and hydrochloric acid were mixed. After one recrystallization from 85% alcohol, the product melted at 279-280°.

Found %: N 3.96; Cl 9.76. $C_{19}H_{21}O_4N \cdot HCl$. Calculated %: N 3.84; Cl 9.7.

Hydrobromide. When an alcohol solution of des-N-methylungerine was made slightly acid by the addition of hydrobromic acid, the hydrobromide was precipitated in the form of needles with m. p. 280-281°. After one recrystallization from 85% alcohol, the product had m. p. 286-287°.

Found %: Br 18.16. $C_{19}H_{21}O_4N \cdot HBr$. Calculated %: Br 19.1.

The picrate had m. p. 243-246°.

Found %: N 10.28. $C_{19}H_{21}O_4N \cdot C_6H_3O_7N_3$. Calculated %: N 10.06.

Iodomethylate. 1 g of des-N-methylungerine was dissolved in methanol by boiling. To this solution was added 2 ml of methyl iodide. After boiling for 30 minutes, the solution was cooled slowly to deposit the iodomethylate of des-N-methylungerine with m. p. 265-266°. After 2 recrystallizations from methanol, the product had m. p. 270-271°. The iodomethylate of de-N-methylungerine was subjected to Hofmann degradation by the same method as for the iodomethylate of ungerine. The des-N-methylungerine was recovered.

Oxidation of des-N-methylungerine. 2 g of des-N-methylungerine was dissolved in 200 ml of acetone and to the solution was added 640 ml of a 1% solution of potassium permanganate in acetone at 14-20°. When all the permanganate solution had been added, the excess of the latter was decolorized on standing. The manganese dioxide hydrate precipitate was removed by filtration. The residue on the filter was washed with potassium hydroxide solution and hot water. The aqueous filtrates were acidified with hydrochloric acid and extracted with ether. Removal of the ether left 0.5 g of a yellow crystalline mass, which melted at 118-119° after 3 vacuum sublimations. A mixed melting point with benzoic acid was not depressed.

Action of AgOH on the iodomethylate of dihydroungerine. 2.8 g of the iodomethylate of dihydroungerine was dissolved in methanol. To the solution was added the calculated amount of freshly precipitated silver oxide, obtained from 1 g of silver nitrate. The mixture was shaken until the solution no longer gave a reaction for halide and then the reaction mixture was heated under reflux on a water bath for 1 hour. The precipitate of silver iodide was removed by filtration and the alcohol evaporated. The residual oily mass was dried in vacuum at 100-105° (10 mm) and the picrate of des-N-methyldihydroungerine with m. p. 239-240° (with decomp.) prepared from it.

Found %: N 10.12. $C_{26}H_{30}O_{12}N_4$. Calculated %: N 9.48.

Des-N-methyldihydroungerine nitrate. An alcohol solution of des-N-methyldihydroungerine was made slightly acid by the addition of concentrated nitric acid. On standing, the solution deposited rosettes of needles. The nitrate had m. p. 182-183° (with foaming).

Found %: N 6.58; OCH_3 7.3. $C_{20}H_{27}O_5N \cdot NHO_3$. Calculated %: N 6.60; OCH_3 7.3.

Iodomethylate. 0.85 g of des-N-methyldihydroungerine was dissolved in methanol. To the solution was added 1 ml of methyl iodide. The iodomethylate precipitated immediately. The m. p. was 297-298° (from methanol).

SUMMARY

1. Distillation of ungerine with zinc dust yielded phenanthridine; oxidation of ungerine with potassium permanganate formed hydrastic acid.

2. During Hofmann degradation, a second double bond appeared in the tetrahydrobenzene ring B in the ungerine molecule and a third double bond was formed due to elimination of a methoxyl group in the form of methyl alcohol; as a result the ring was aromatized. This was established by the fact that benzoic acid was obtained by the oxidation of des-N-methylungerine.

3. Ungerine is a phenanthridine derivative with a methylenedihydroxy group in position 6-7. The double bond is most probably between carbon atoms 1-2 and the methoxy group in position 3.

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INVESTIGATION OF ACONITE ALKALOIDS

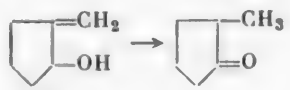
XIV. STRUCTURE OF THE ALKALOID ZONGORINE

A. D. Kuzovkov

S. Ordzhonikidze All-Union Chemico-Pharmaceutical Scientific Research Institute

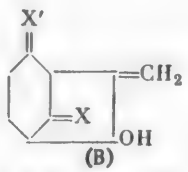
In a previous communication [1] it was suggested that zongorine and napellonine, which was recently isolated by Wiesner et al. [2], were identical. This hypothesis was confirmed by direct comparison of the two substances.*

Zongorine, $C_{22}H_{31}O_3N$, contains a terminal methylene group, $-C = CH_2$ [1, 2], a Co group in a six membered ring (ν 1708 cm^{-1} in the infrared spectrum), two hydroxyls [3] and a $C-CH_3$ group [2]. Oxidation of the alkaloid with lead tetraacetate yielded glyoxal [2], indicating the presence of the group $N-CH_2CH_2OH$. Together with dihydrozongorine, the hydrogenation of zongorine formed a substance isomeric with zongorine [4], which contained two keto groups: one of these was in a six-membered ring [1708 cm^{-1}) and the other in a five-membered one (1740 cm^{-1}). The formation of the isomer was explained [4] by disproportionation of all allyl hydroxyl group.



(A)

A study of the ultraviolet absorption spectrum of the alkaloid [2] and comparison [1] of its absorption spectra with the spectra of derivatives in which the double bond had been hydrogenated or the keto group reduced led to the conclusion that a β, γ-unsaturated keto group in a six-membered ring was present. This makes it possible to change partial formula (A) to partial formula (B).



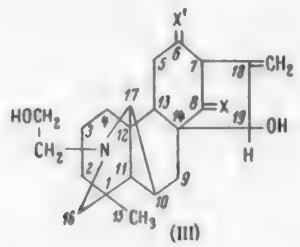
(B)

X = H_2, X' = O or
X = O, X' = H_2.

The mixture of products from dehydrogenation of the alkaloid with selenium yielded 1,10-dimethyl-7-ethylphenanthrene (I) [1] and 1-methyl-7-ethyl-3-azaphenanthrene (II) [2]. The elucidation of the nature of these two substances, the properties of zongorine considered above and its similarity to alkaloids of the garryine

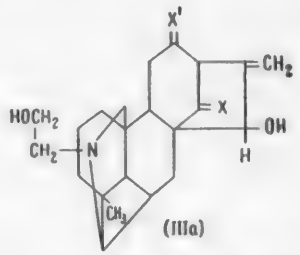
*We are very grateful to Prof. K. Wiesner for the sample of napellonine he supplied and also for the extremely valuable discussion of the problem of studying the structure of this alkaloid.

(see formula below) and atisine groups all lead to the hypothesis that the structure of zongorine may be expressed by one of two formulas, namely, (III) or (IIIa).



(III)

(X=O, X'=H$_2$ или X=H$_2$, X'=O)



(IIIa)

(X=O, X'=H$_2$ или X=H$_2$, X'=O).

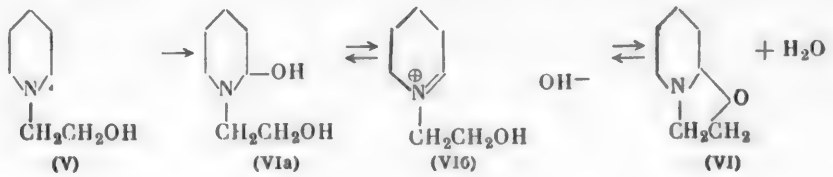
In the present article, formulas (III) and (IIIa) are discussed on the basis of newly obtained data.

In the catalytic hydrogenation of diacetylzongorine, not only was the double bond saturated, but part of the substance underwent hydrogenolysis with replacement of an acetoxy group by hydrogen: after hydrolysis of the mixture of reaction products, dihydrozongorine (IV) and dihydrodesoxyzongorine (V) with the composition $C_{22}H_{33}O_2N$ were isolated. The possibility of hydrogenolysis [5] confirms the presence of the allyl grouping CH(OH)-C = CH_2 in zongorine.

Oxidation of dihydrodesoxyzongorine (V) with chromium trioxide in pyridine yielded substance (VI) with the composition $C_{22}H_{31}O_2N$ and substance (VII) with the composition $C_{22}H_{33}O_3N$. Substance (VI) contained one carbonyl group (1700 cm^{-1}), did not contain a hydroxyl group, was converted into dihydrodesoxyzongorine (V) by catalytic reduction and was oxidized by $KMnO_4$ to a lactam (VIII) with the composition $C_{22}H_{31}O_3N$, whose infrared spectrum showed the bands of a keto group (1708 cm^{-1}), a lactam carbonyl in a six-membered ring (1613 cm^{-1}) [6] and a hydroxyl group. The lactam (VIII) contained one OH group.

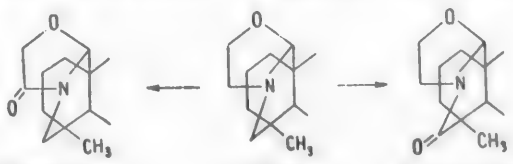
Oxidation of dihydrozongorine (IV) with chromium trioxide did not yield the expected diketone, but instead substance (IX) with the composition $C_{22}H_{31}O_3N$, containing one keto group (1700 cm^{-1}). Catalytic reduction of (IX) led to dihydrozongorine (IV) and oxidation with $KMnO_4$ to the lactam (X) $C_{22}H_{31}O_4N$, which contained a keto group (1690 cm^{-1}) and a lactam carbonyl in a siz-membered ring (1610 cm^{-1}).

The formation of (VI) may be represented as the result of oxidation of a CH_2 or CH group, in a position α to a nitrogen, to a CHOH or COH group. The pseudo base (VIa), obtained by such an oxidation, may be reversibly converted into a Schiff's base (VIb) and then into an oxazolidine derivative (VI). Oxazolidine (IX) is formed analogously. [The partial formulas of compounds (V), (VIa), (VIb) and (VI) are given in the scheme below].



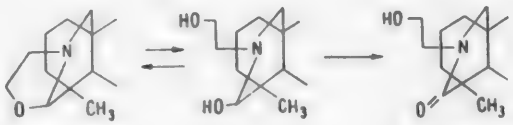
(V) (VIa) (VIб) (VI)

As is known, the oxidation of alkaloids containing an oxazolidine ring with potassium permanganate may proceed in two directions. The oxidation of atisine [6] yielded α- and β-oxoatisines, containing unruptured oxazolidine rings.



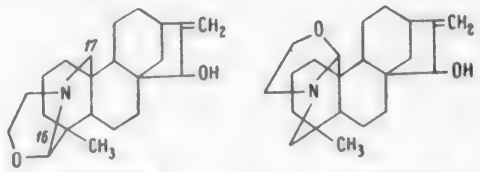
α-Oxoatisine Atisine β-Oxoatisine

Isoatisine was oxidized to oxoisoatisine [6] with rupture of the oxazolidine ring. Apparently, on solution of isoatisine, part of the substance is converted into the equilibrium form of the pseudo base and is then oxidized to a lactam.



Isoatisine Oxoisoatisine

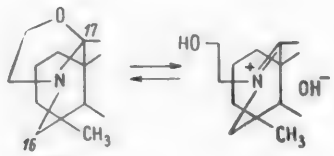
Oxazolidines (VI) and (IX) are oxidized to lactams (VIII) and (X) in the same way that isoatisine is oxidized to oxoisoatisine. Dihydrodesoxyzongorine (V) and dihydrozongorine (IV) may be oxidized by $KMnO_4$ directly to lactams (VIII) and (X). From what has been said it follows that the oxazolidine ring in oxazolidines (VI) and (IX) is formed by oxidation of a $>CH_2$ group next to a nitrogen and not a $\gtrless$ CH group. This $>CH_2$ group may be either in position 16 (formula III) or in position 17 (formula IIIa). In the first case the oxazolidines (VI) and (IX) must be analogous to garryine and in the second, to veatchine. For solving the problem of the position of attachment of the oxazolidine ring, a comparison of the strengths of bases has been used many times [7]. Thus, for example, garryine (pK 8.7) differs sharply in this respect from veatchine (pK 11.5). The basicity of oxazolidine (VI) (pK 8.3 in 50% methanol) is close to that of garryine, which indicates the presence of a C_{16}-oxazolidine ring in compound (VI) and excludes formula (IIIa).



Garryine Veatchine

The comparatively high basicity of veatchine, atisine and cuauchichicine is explained [8] by the tendency of C_{17} to assume a "trigonal state" (with the formation of a double bond $C_{17} = N^+ <$) due to steric hindrance of the H-atom at it.

K. Wiesner et al. [2] studied the silver oxide oxidation of tetrahydrozongorine (XI), which was obtained by reduction of the keto group in the alkaloid to a hydroxyl by means of lithium aluminum hydride and catalytic hydrogenation of the double bond. After the oxidation, a substance with the composition $C_{22}H_{33}O_3N$, m.p. 220° and 6.77 was isolated. It did not contain carbonyl groups and was a Schiff's base. Formula (XII) was proposed for this substance on the basis of its oxidation with CrO_3 into an oxazolidine lactam, which had a lactam group in a six-membered ring (1642 cm^{-1}) and an unruptured oxazolidine ring. It might be expected that oxidation with Ag_2O would lead to C_{17}-oxazolidines. However, we were unable to confirm this. Oxidation of tetrahydrozongarine [XI] with Ag_2O yielded substance (XIIa), whose composition and constants corresponded to those of oxazolidine (XII). Like the analogy in the preparation methods, this indicates the identity of (XII) and (XIIa).

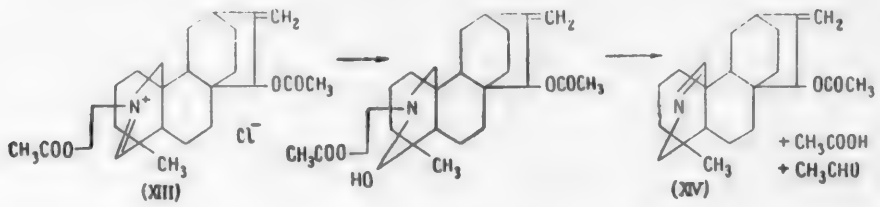


(XII)

Under the action of CrO_3, oxidation of the hydroxyl group at the sixth carbon atom in compound (XIIa) led to the formation of oxazolidine (IX), indicating the presence of an oxazolidine ring at C_{16} in substance (XII).

Oxidation of tetrahydrozongorine (XI) with chromium trioxide gave oxazolidine (IX). On oxidation of (XI), Wiesner obtained a substance $C_{22}H_{35}O_4N$ together with (XII). Apparently, like substance (VII), this substance contains a hydroxyl group at C_{17}.

Recently D. Dvornik and O. Edwards reported [9] that by acetolysis of isoatesine they obtained the diacetate hydrochloride (XIII). When heated in boiling chloroform, the base isolated from the diacetate hydrochloride (XIII) was cleaved to the azomethine (XIV).



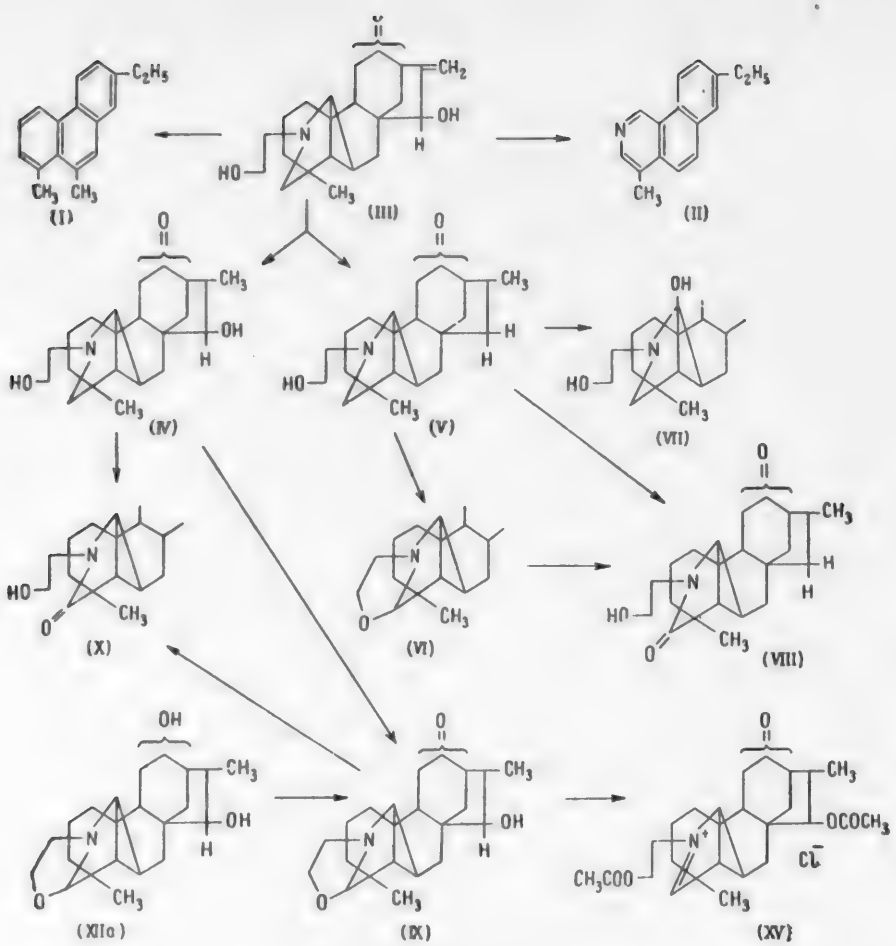
It seemed interesting to test the possibility of an analogous cleavage with the oxazolidine (IX). Were a substance similar to the azomethine (XIV) obtained, it would throw doubt on the accuracy of formula (III) for zongorine, since in this case we would have to assume the formation of a double bond between C_{17} and one of the neighboring carbon atoms, which is contrary to Bredt's rule. From oxazolidine (IX) we obtained a diacetate hydrochloride (XV); the base isolated from it was unchanged by heating in boiling chloroform for 50 minutes. After the product had been heated for 14 hours in an autoclave at 100° and then for 24 hours at 120°, it was possible to isolate the unchanged substance. The results of this experiment show the stability of diacetate (XV), which may depend on the presence of the tertiary C_{17}.

Previously S. Yu. Yunusov [3] described the cleavage of zongorine under the conditions of the Hofmann degradation. We also reported [10] the cleavage of aconitane, a conversion product of zongorine, under these conditions. Formula (III) does not allow for such a reaction and this compelled us to study the latter.

Treatment of the iodomethylate of dihydrozongorine with Ag_2O yielded a quaternary base, which was heated at 150° in a vacuum of 0.2 mm. The reaction product (XVI), which had the composition $C_{22}H_{33}O_3N$, did not differ from dihydrozongorine. The substance did not decolorize a sulfuric acid solution of permanganate, and was not changed by shaking in alcohol solution with a Pt catalyst under a slight excess pressure of hydrogen at 20°. As has now been established, the "des-N-methylaconitane" (XVII) obtained previously [10] had similar properties. These observations compel one to think that compounds (XVI) and (XVII) are not des-bases and do not contain a double bond, but are isomers of dihydrozongorine and aconitane, respectively. To confirm the presence of an unchanged nitrogen-containing ring in base (XVI), this base was oxidized with $KMnO_4$ in acetone and CrO_3 in pyridine. In the first case lactam (XVIII) with the composition $C_{22}H_{31}O_4N$ was obtained. In the IR spectrum of this substance, the absorption band of the lactam carbonyl was in the same region (1613 cm^{-1}) as in lactam (X) 1610 cm^{-1}). The second reaction yielded oxazolidine derivative (XIX), analogous to oxazolidine (VI).

After the reaction of zongorine with benzaldehyde with boiling in a methanol solution of sodium methylate, we isolated the product of aldol addition of benzaldehyde to zongorine, $C_{22}H_{30}O_3N \cdot CH(OH)C_6H_5$ (XX), whose formation could be caused by the presence of a CH_2 group next to a CO group, and in the absence, the presence of a CH group. The latter seems more probable since in the other case the stability of (XX) towards dehydration when heated with a concentrated solution of sodium alcoholate is not understandable [11]. However, this stability may be caused by some type of steric hindrance. Therefore, as yet the problem of the position of the keto group in zongorine cannot be solved unequivocally.

In conclusion, we should draw attention to the stability of the hydroxyl at C_{19} to the oxidative action of CrO_3 in pyridine. Apparently, this is connected with the steric position of this hydroxyl group.



EXPERIMENTAL

Reduction of diacetylzongorine. Preparation of dihydrozongorine (IV) and dihydrodesoxyzongorine (V). To a solution of 20 g of zongorine in 40 ml of pyridine was added 30 g of acetic anhydride. The solution was kept at 20° for 14 hours and then evaporated to dryness in vacuum. The crystalline residue was washed with ether, dried and dissolved in 100 ml of water by the addition of acetic acid. The solution was shaken with a Pt catalyst (from 0.2 g of PtO_2) under a slight excess pressure in an atmosphere of hydrogen. After 2 hours, about 1.5 moles of hydrogen had been absorbed. The catalyst was removed by filtration, the filtrate evaporated to dryness and the residue dissolved in 200 ml of methanol. After the addition of 25 ml of 40% potassium hydroxide, the solution was boiled for 1 hour, then evaporated to dryness and diluted with water and the crystalline residue collected by filtration. After being dried, the precipitate was dissolved in boiling benzene. Evaporation of the solution to small volume yielded 8 g of dihydrozongorine (IV) with m. p. 206-208° and R_f 0.47.

After isolation of the dihydrozongorine, the mother solution was passed through a column with Al_2O_3. Elution with chloroform yielded 2.7 g of dihydrodesoxyzongorine (V) with m. p. 184-187° (from acetone) and R_f 0.62.

Found %: C 76.60; H 9.70; N 4.08. $C_{22}H_{33}O_2N$. Calculated %: C 76.92; H 9.69; N 4.08.

Elution of the column with a mixture of chloroform and methanol (9 : 1) yielded 2.5 g of dihydrozongorine.

Oxidation of dihydrodesoxyzongorine (V). a) To oxazolidine (VI). To a solution of 0.5 g of (V) in 5 ml of pyridine was added a mixture obtained by adding 0.5 g of CrO_3 to 5 ml of pyridine at 20°. After 14 hours, the mass was diluted with twice the amount of water, made strongly alkaline with 40% NaOH and extracted with

ether. The extract was dried with sodium sulfate and evaporated (finally in vacuum). The residue was dissolved in 5% hydrochloric acid; the solution was decolorized with charcoal, made alkaline and extracted with ether; when the ether extract was evaporated to small volume, it deposited a small amount of crystalline base (VII) with m. p. 281-282° (from a mixture of methanol and acetone) and R_f 0.62.

Found %: C 73.81; H 8.85. $C_{22}H_{33}O_3N$. Calculated %: C 73.50; H 9.25. (After drying at 130° and 0.03 mm).

After isolation of (VII) the mother solution was evaporated, the residue dissolved in boiling hexane, boiled with charcoal and the solution filtered; cooling the solution yielded substance (VI) with m. p. 112-114° and R_f 0.48. Its infrared spectrum showed the band of a CO group (1700 cm^{-1}); OH group bands were absent.

Found %: C 77.36, 77.64; H 9.18, 9.14. $C_{22}H_{31}O_2N$. Calculated %: C 77.39; H 9.15.

Catalytic reduction of oxazolidine (VI) in alcohol solution with Pt (from PtO_2) yielded a substance with m. p. 184-187° (from acetone); a mixture of this with dihydrodesoxyzongorine melted at the same temperature.

b) To lactam (VIII). To 0.5 g of (V) in 50 ml of acetone and 0.5 ml of acetic acid was added 1.5 g of powdered $KMnO_4$ in portions over 4-6 hours. After 24 hours, the solution was filtered and evaporated. The residue was dissolved in ether. The base was extracted by shaking with 5% sulfuric acid. Evaporation of the ether solution yielded 0.1 g of neutral substance, which melted at 252-253° (in vacuum at 0.2 mm) after recrystallization from acetone. The infrared spectrum contained the following bands: OH (3400 cm^{-1}); keto group (1708 cm^{-1}) and lactam carbonyl (1613 cm^{-1}).

Found %: C 73.88, 74.00; H 8.53, 8.63; OH 4.69. $C_{22}H_{31}O_3N$. Calculated %: C 73.93; H 8.74; 1 OH 4.77.

Oxidation of oxazolidine (VI) with potassium permanganate in acetone under the conditions described above yielded a neutral substance with m. p. 249-250° (in vacuum) and a mixture with lactam (VIII), which had m. p. 252-253°, melted at 250-251°. The substances had identical infrared spectra.

Oxidation of dihydrozongorine (IV). a) To lactam (X). 0.8 g of dihydrozonogrine was oxidized with $KMnO_4$ under the condtions presented above. A neutral substance was obtained, which was recrystallized from acetone and then from aqueous alcohol. The substance shrank at 297° and melted at 302-305°. The infrared spectrum had the bands of an OH (3400 cm^{-1}), a keto group in a six-membered ring (1690 cm^{-1}) and a lactam carbonyl (1610 cm^{-1}).

Found %: C 71.08, 71.06; H 8.30, 8.45; N 4.04. $C_{22}H_{31}O_4N$. Calculated %: C 70.60; H 8.37; N 3.75.

b) To oxazolidine (IX). 5 g of dihydrozongorine in 50 ml of pyridine was oxidized with 5 g of CrO_3 in 100 ml of pyridine. The reaction product was dissolved in a large amount of boiling aqueous acetone; evaporation to a volume of about 20 ml yielded 2.5 g of base with m. p. 240-242° and R_f 0.34.

Found %: C 73.88, 74.34; H 8.77, 8.87. $C_{22}H_{31}O_3N$. Calculated %: C 73.93; H 8.74.

The hydrochloride was prepared in alcohol solution and on addition of ether, it precipitated as a crystalline substance with m. p. 293°.

0.8 g of oxazolidine (IX) was oxidized with $KMnO_4$ in acetone solution. The neutral reaction product crystallized on heating with aqueous acetone and had m. p. 302-304°; a mixed melting point with lactam (X) was not depressed.

Acetolysis of oxazolidine (IX). Preparation of diacetate hydrochloride (XV). 1.3 g of oxazolidine (IX) hydrochloride was dissolved in 40 ml of a mixture of acetic anhydride and acetic acid (1 : 1). The solution was heated for 4 hours at 80° and then evaporated to dryness in vacuum. The addition of acetone to the residue yielded 1.2 g of a crystalline substance, which was recrystallized from a mixture of alcohol and ether. The m. p. was 296-298° and the R_f 0.32. The melting point of a mixture with the hydrochloride of oxazolidine (IX) was depressed by 5°.

Found %: C 66.05, 65.94; H 7.67, 7.79; N 3.00. $C_{26}H_{36}O_5NCl$. Calculated %: C 65.31; H 7.59; N 2.93.

0.5 g of the diacetate hydrochloride (XV) was dissolved in 10 ml of ice-water and shaken with 10 ml of cooled chloroform; then to the mixture was added 4 ml of 20% KOH solution, cooled to 0°. The mixture was shaken for 1 minute and the chloroform layer then separated. The aqueous solution was extracted twice with chloroform (15 ml portions). The extracts were dried with sodium sulfate and boiled for 50 minutes while 2/3 of the solvent slowly distilled. The solution was then evaporated to dryness in vacuum. Paper chromatography showed the absence of any conversion products of (XV). The base was then dissolved in chloroform and heated for 14 hours in a bomb at 100° and for 24 hours at 120°. After evaporation of the chloroform solution, the residue was dissolved in acetone. Addition of an alcohol solution of HCl precipitated a hydrochloride, which, after recrystallization from a mixture of alcohol and ether, melted at 293° and did not depress the melting point of the diacetate hydrochloride (XV).

Experiment on the Hofmann degradation of dihydrozongorine (IV). 8 g of (IV) and 30 ml of methyl iodide were heated in a bomb for 14 hours at 100°. We obtained 10 g of the iodomethylate with m. p. 266°.

Found %: I 25.30. $C_{23}H_{36}O_3NI$. Calculated %: I 26.00.

10 g of the iodomethylate was dissolved in 800 ml of water with heating. The solution was shaken for 15 minutes with excess silver oxide. The silver iodide was removed by filtration. filtrate evaporated to dryness in vacuum and the residue heated at 150° in a vacuum of 0.2 mm until the evolution of volatile materials ceased. The reaction product was dissolved in acetone and evaporation of the solution to small volume crystallized 4 g of the base (XVI) with m. p. 228-230° and R_f 0.44. The substance did not decolorize a sulfuric acid solution of $KMnO_4$ and did not absorb hydrogen when shaken with Pt (from PtO_2) in alcohol solution at 20° with a slight excess pressure of hydrogen.

Found %: C 73.48; H 9.02; N 3.84; OH 10.5. $C_{22}H_{33}O_3N$. Calculated %: C 73.50; H 9.25; N 3.89; 2 OH 9.46.

0.5 g of the base (XVI) was oxidized with CrO_3 in pyridine. We obtained 0.2 g of (XIX) with m. p. 278-280° (from acetone) and R_f 0.28.

Found %: C 73.72; H 8.66; OH 4.64. $C_{22}H_{31}O_3N$. Calculated %: C 73.93; H 8.74; 1 OH 4.76.

Catalytic reduction of 0.05 g of (XIX) in 20 ml of alcohol with Pt (from PtO_2) yielded a substance with m. p. 226-228°, which did not depress the melting point of the base (XVI).

0.5 g of (XVI) was oxidized with $KMnO_4$ in acetone. We obtained a neutral substance (XVIII) with m. p. 302° (from acetone). On admixture with lactone (X), the melting point was depressed. The substance contained an OH group (3400 cm^{-1}), a keto group (1690 cm^{-1}) and a lactam carbonyl (1613 cm^{-1}).

Found %: C 70.74, 70.61; H 8.53, 8.10. $C_{22}H_{31}O_4N$. Calculated %: C 70.60; H 8.37.

Condensation of zongorine with benzaldehyde. 0.7 g of zongorine, 0.5 ml of benzaldehyde, 4 ml of methanol and 5 ml of CH_3ONa solution (from 50 ml of methanol and 4 g of sodium) were mixed and boiled for 15 minutes. The mixture was then evaporated to dryness in vacuum, water and ether added to it, the mixture shaken and the ether layer separated, washed with water, dried and evaporated. To a solution of the residue in 1% HCl was added perchloric acid. The perchlorate was collected by filtration, washed with water and dried in vacuum. The perchlorate of (XX) decomposed above 310°; its infrared spectrum contained the band of an isolated keto group (1700 cm^{-1}). From the perchlorate we obtained the amorphous base, which was dried at 100° and 0.04 mm.

Found %: C 75.77, 75.61; H 8.10, 8.12. $C_{29}H_{37}O_4N$. Calculated %: C 76.14; H 8.05.

Comparison of napellanine with zongorine. The sample of napellonine we obtained from K. Weisner melted at 200-201°; in their article, K. Weisner et al. reported m. p. 212° for napellonine. A mixture with zongorine (m. p. 199-200°) melted at 199-200°. The absorption spectra of the substances in the infrared coincided.

Preparation and oxidation of tetrahydrozongorine (XI). 0.9 g of dihydrozongorine (IV) was reduced with 0.9 g of $NaBH_4$ in methanol solution (2 hours at 0°, 12 hours at 20°, and 1 hour boiling) to yield 0.7 g of tetrahydrozongorine (XI) with m. p. 162.5-164° (m. p. 158° in the literature [2]) and R_f 0.67.

Oxidation of tetrahydrozongorine (XI) with chromium trioxide in pyridine yielded a substance with m. p. 238.5-240.5°. A mixture with oxazolidine (IX) melted at the same temperature.

0.6 g of (XI), 30 ml of methanol and Ag_2O (from 3.6 g of $AgNO_3$) was boiled for 2 hours and the solution then filtered and evaporated. The residue was dissolved in 5% hydrochloric acid, decolorized with charcoal, made alkaline and extracted with ether. We obtained 0.5 g of base (XIIa) with m. p. 206-208° (from a mixture of acetone and methanol) and R_f 0.41. M. p. 220° is reported in the literature [2] for (XII). However, it should be noted that in determining the melting point of a sample of napellonine we obtained a value that was 10° below that reported by K. Weisner at al. Apparently, this discrepancy depends on the method of determining the melting point.

Found %: C 73.43, 73.45; H 9.08, 9.27. $C_{22}H_{33}O_3N$. Calculated %: C 73.50; H 9.25.

50 mg of (XIIa) was oxidized with CrO_3 in pyridine. We obtained a base with m. p. 234-236° (from acetone). A mixture with oxazoline (IX) melted at the same temperature. The substance had identical infrared absorption spectra.

Paper chromatography was carried out at 20° with a butanol – water – 5% acetic acid system.

SUMMARY

1. The identity of napellonine and zongorine was established.

2. The changed formula for zongorine we proposed previously was discussed on the basis of newly obtained data. It was confirmed that the zongorine molecule contains an allyl hydroxyl group, a saturated, substituted piperidine ring, a CH_2 group in position 16 and a CH group (the position of condensation of two rings) in position 17. The possibility of the keto group of zongorine being in position 8 was demonstrated. It was shown that zongorine derivatives do not undergo a Hofmann degradation.

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PHYSICOCHEMICAL ANALYSIS OF THE INTERACTION OF AMINES AND ACIDS

V. THERMAL ANALYSIS OF THE TERNARY SYSTEM UREA – TRICHLOROACETIC ACID – WATER

M. N. Kuznetsova and M. M. Shul'man

Technological Institute of the Meat and Milk Industry, Moscow

The chemistry of urea is being developed intensively at the present time and this is explained on the one hand by its role in the life of living organisms and, on the other, by its value in the national economy. Urea is a valued nitrogen-containing fertilizer and it is also used in the production of carbamide resins and in the pharmaceutical industry. A unique property of urea is its capacity for selective adsorption of straight-chain organic compounds present in mixtures with branched-chain compounds [1], and this increases the interest in studying the chemistry of urea even more.

It is known that urea gives salt-like compounds with monobasic acids and these are predominantly of two types, namely equimolecular and of the 1 : 2 type (two molecules of acid). The stronger acids [HCl, HNO_3, CCl_3COOH, $C_6H_2OH(NO_2)_3$] give compounds of the first type [2] and the weaker ones (HCOOH, $CH_2ClCOOH$) – give both types [3, 4]. With a decrease in the strength of the acid, the 1 : 2 type of compound [for example $CO(NH_2)_2 \cdot 2CH_3COOH$, $CO(NH_2)_2 \cdot 2C_2H_5COOH$]; begins to predominate; finally, in the fatty acid series, beginning with butyric acid, compounds with urea capable of crystallizing are not formed [5]. There are references in the literature to the fact that certain compounds of urea with acids are decomposed by water [2]. The problem of the action of water on the compounds given above has not been studied sufficiently. We previously showed that compounds of urea with formic acid of both types and with acetic acid of the 1 : 2 type are stable in the presence of water [3, 6].

The aim of the present work was to investigate the effect of water on compounds of urea with trichloroacetic acid.

The visual method of thermal analysis was used in the work. In temperature regions below 0°, we worked with an alcohol thermometer, which made it possible to determine the temperature with an accuracy of ± 0.2 – 0.3°, and in regions above 0°, a thermometer with 0.1° graduations was used. The mixtures usually crystallized well and the difference between the appearance temperature and the melting point of crystals did not exceed 0.3-0.5°. The urea had m. p. 132.7° and the trichloroacetic acid, 57.5°. All the compositions are expressed in molar percents.

The melting point of the binary systems water – urea, water – trichloroacetic acid and urea – trichloroacetic acid was investigated previously by other authors [1, 7, 8]. In the first two systems, compounds were not detected and the melting point diagrams had the simplest form with a eutectic point. An equimolecular compound with a sharp maximum was detected in the third system. We studied all these three systems again and our results did not differ essentially from literature data.

We studied the melting point diagrams of nine sections inside the diagram of the ternary system.

1) 10% CCl_3COOH + 90% H_2O → $CO(NH_2)_2$
2) 20% CCl_3COOH + 80% H_2O → $CO(NH_2)_2$
3) 30% CCl_3COOH + 70% H_2O → $CO(NH_2)_2$
4) 50% CCl_3COOH + 50% H_2O → $CO(NH_2)_2$
5) 80% CCl_3COOH + 20% H_2O → $CO(NH_2)_2$
6) 20% $CO(NH_2)_2$ + 80% CCl_3COOH → H_2O
7) 50% $CO(NH_2)_2$ + 50% CCl_3COOH → H_2O
8) 5% $CO(NH_2)_2$ + 95% H_2O → CCl_3COOH
9) 20% $CO(NH_2)_2$ + 80% H_2O → CCl_3COOH

The data from investigating these sections are illustrated graphically in Figs. 1 and 2.

As a result of the investigation, we constructed a projection diagram of the triple system and plotted isotherms at 10° intervals (Fig. 3). The diagram consists of four crystallization fields: three fields for the pure components and one field for the compound $CO(NH_2)_2 \cdot CCl_3COOH$. Section 7 corresponds to the quasibinary system $CO(NH_2)_2 \cdot CCl_3COOH - H_2O$ with a eutectic point at −1.2°, lying at 97% H_2O. This

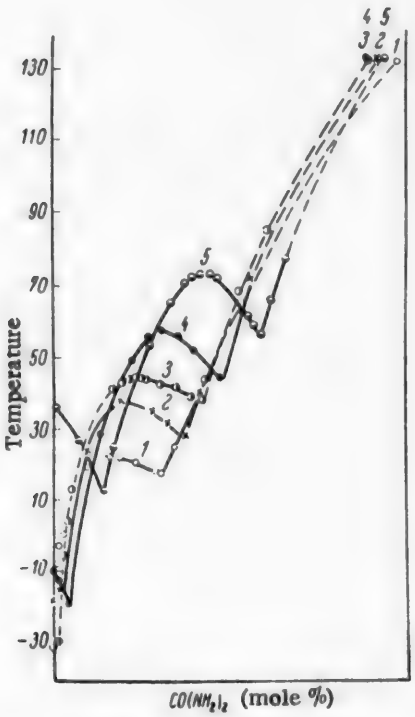

Fig. 1. Melting point diagrams of section 1-5 of the triple system urea – trichloroacetic acid – water.

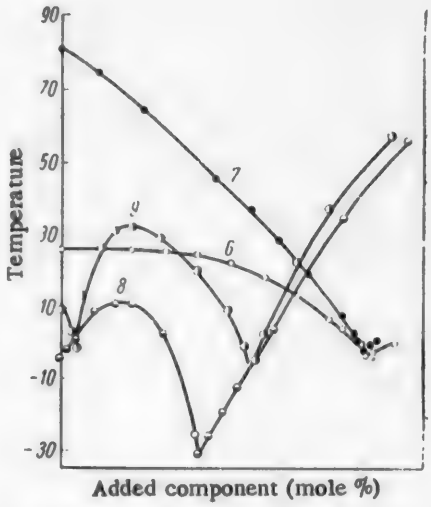

Fig. 2. Melting point diagram of sections 6-9 of the triple system urea – trichloroacetic acid – water.

cross-section divides the diagram into two ternary systems: 1) $CCl_3COOH - H_2O - CO(NH_2)_2 \cdot CCl_3COOH$ and 2) $H_2O - CO(NH_2)_2 - CO(NH_2)_2 \cdot CCl_3COOH$.

In the first system, the triple eutectic point lies at -38.3° and has the composition 33.5% trichloroacetic acid, 65.% water and 1.5% urea. In the second system, the triple eutectic point lies at -12.5° and has the composition 1.5% trichloroacetic acid, 85.0% water and 13.5% urea.

On the projection diagram, the crystallization fields occupy the following fractions of the area of the triangle: ice 1.3%, trichloroacetic acid 12.6%, urea 25.3% and the compound $CO(NH_2)_2 \cdot CCl_3COOH$ 60.8%.

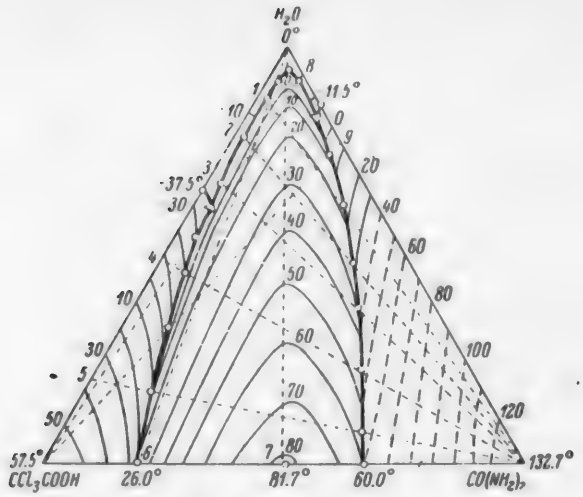

Fig. 3. Melting point diagram of the triple system urea – trichloroacetic acid – water. Explanation in text.

The large area of the field occupied by the compound and the course of the isotherms show that this compound is stable in the presence of water. In this respect the given compound behaves similarly to the compounds of urea with formic [3] and acetic acids [6].

SUMMARY

1. An investigation was made of the melting point diagram of the ternary system urea – trichloroacetic acid – water. It was established that the compound $CO(NH_2)_2 \cdot CCl_3COOH$ is stable in the presence of water. Its field occupies 60.8% of the area of the diagram of the ternary system.

2. The $H_2O - CO(NH_2)_2 \cdot CCl_3COOH$ section divides the diagram into two ternary systems: a) $CCl_3COOH - H_2O - CO(NH_2)_2 \cdot CCl_3COOH$ with a eutectic point at -38.3° and b) $H_2O - CO(NH_2)_2 \cdot CCl_3COOH$ with a eutectic point at -12.5°.

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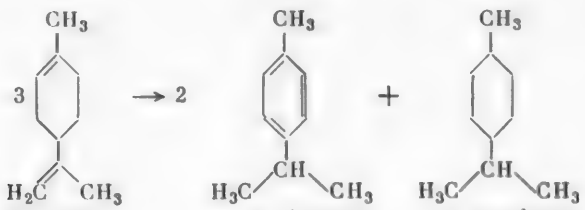
REASONS FOR THE ACTIVITY AND DEACTIVATION OF RANEY NICKEL IN IRREVERSIBLE CATALYSIS

G. L. Dranishnikov

Archangel Wool Technology Institute

In a previous communication [1] it was shown that Raney nickel is a highly active catalyst in irreversible Zelinskii catalysis: when boiled (175-178°) with Raney nickel, dipentene is quantitatively converted into a mixture of p-cymene and p-menthane in a ratio of 2 : 1. Similar conversions are also undergone on the same catalyst by other monocyclic terpenes and mixtures of them in the liquid phase and also by the bicyclic terpenoid hydrocarbon, α-pinene, in the vapor phase [2]. During the investigation it was noticed that the catalyst used did not show initial activity in work with freshly distilled terpenes and the irreversible catalysis of terpenes, sotred in contact with air, did not proceed to completion or did not occur at all.

The literature throws very little light on the reasons for the activity and the mechanism of action of different catalysts for irreversible catalysis. There is only the investigation of N. D. Zelinskii [3] on the reasons for the activity of palladium deposited on asbestos in irreversible catalysis: oxygen and hydrogen were removed successively from palladized asbestos, and palladium black in a pure form showed a high activity. Hence, N. D. Zelinskii considered it a catalytic agent in irreversible catalysis. This conclusion is not unexpected if we consider the peculiarities of an irreversible catalytic reaction, consisting of disproportionation of hydrogen between molecules of a substance. For example, for dipentene the reaction scheme (without the intermediate stages) may be represented in the following way:



The role of the catalyst consists of dehydrogenation of 2/3 of the dipentene molecules to cymene and simultaneous hydrogenation of 1/3 of the molecules to menthane with the hydrogen eliminated. A catalyst in irreversible catalysis must consequently show the same high activity both in dehydrogenation and in hydrogenation of the substance.

The presence or absence of hydrogen in the catalyst before the reaction, it would seem, should not affect its activity in irreversible catalysis, as was the case with palladium black in N. D. Zelinskii's investigations. The loss of activity of Raney nickel during irreversible catalysis may be caused by the formation of films of polymeric products on its surface. However, careful washing of the spent catalyst with solvents under conditions excluding the entrance of air, did not restore the catalyst's activity.

We then found that a catalyst that had lost its pyrophoric properties by contact with air was quite incapable of promoting irreversible catalysis and this led to the idea of a connection between the activity of Raney nickel and its hydrogen content.

In investigations on the nature of skeletal catalysts and factors in their catalytic activity in low temperature hydrogenation processes [4-7] a relation was found between the activity of the catalysts and their hydrogen content and the chemical non-equivalence of hydrogen in freshly prepared Raney nickel was demonstrated. Thus, Freidlin and Ziminova [4] found that freshly prepared Raney nickel contained hydrogen in two forms, namely, adsorbed and dissolved (H_{ads} and H_{dis}). According to the data of the authors, the removal of H_{ads} from the catalyst is a reversible process and does not affect the activity of the catalyst in low-temperature hydrogenation. On losing H_{dis}, the catalyst loses the capacity to absorb hydrogen and is deactivated due to rupture of its active structure since H_{dis} is structurally bound to the metal.

Our investigations showed that as a catalyst in irreversible catalysis, Raney nickel differs substantially from palladium black, investigated by N. D. Zelinskii: the activity of Raney nickel also depends on its hydrogen content as occurs in low temperature hydrogenation. Deactivation of Raney nickel is due to partial or complete loss of hydrogen, contained in the freshly prepared catalyst; the activity of the catalyst may be restored by treating it with hydrogen. Thus, if freshly prepared, extremely active catalyst is left in air, together with its pyrophoric properties it loses its activity in irreversible catalysis: this and the former are restored to a considerable extent when the catalyst is heated in a hydrogen atmosphere at 350-400°.

A catalyst, used 2-3 times in an irreversible catalysis reaction, completely loses its activity. After treatment with hydrogen at room temperature or at 350-400°, the activity of the catalyst is restored, the more the longer the treatment.

Loss of hydrogen by the catalyst is possible due to desorption in experiments at comparatively high temperatures (175-178°) and as a result of consumption of hydrogen by the catalyst on side hydrogenation processes. To determine whether the catalyst hydrogen was desorbed during irreversible catalysis, we boiled freshly prepared catalyst for a long period (3-4 hours) with pure menthane (b. p. 170°) and p-cymene (b. p. 178°) in a carbon dioxide atmosphere. After such treatment, the activity of the catalyst had not fallen. Hence, it follows that during irreversible catalysis desorption does not occur and neither does hydrogenation of the p-cymene formed by hydrogen of the catalyst.

It must be admitted that dehydrogenation of the catalyst proceeds due to the simultaneously occurring hydrogenation of the starting hydrocarbon or intermediate products and is a process accompanying irreversible catalysis. This is also confirmed by experiments on irreversible catalysis with a catalyst dehydrogenated chemically by the procedure developed by Freidlin and Rudneva [6]. For this purpose, Michler's ketone and nitrobenzene were used: the former removes H_{ads} and the latter, H_{ads} and H_{dis}. A catalyst dehydrogenated with nitrobenzene and thus having lost H_{ads} and H_{dis} is inactive in irreversible catalysis; after treatment with hydrogen at 350-400°, it partially recovers its activity. The activity of a catalyst, dehydrogenated with Michler's ketone and lacking H_{ads}, though retained, is considerably less than that of fresh catalyst and is lower, the longer the treatment with Michler's ketone; nonetheless, even after very long treatment, the catalyst still remains active. Consequently, the main reason for deactivation of Raney nickel during irreversible catalysis is the loss of dissolved (structurally bound) hydrogen from the catalyst.

The activity of Raney nickel in irreversible catalysis is also strongly affected by the presence of even very small amounts of peroxide compounds in the substance: if a freshly distilled mixture of terpenes is left for 3-4 days without protection from the air, then the catalysis of such a mixture proceeds considerably more slowly or does not even proceed at all. If the peroxides are removed from a such a mixture of terpenes, then the catalysis proceeds normally. The most efficient method of purifying terpenes from peroxides is steam distillation. In this case, deactivation of the catalyst is caused by the fact that the peroxide repidly dehydrogenates the catalyst.

EXPERIMENTAL*

The Raney nickel catalyst was prepared by complete extraction of a nickel-aluminum alloy (52% nickel) with subsequent washing of the prepared catalyst with water until neutral to phenolphthalein, as described previously [1]. The catalyst was stored under alcohol.

For the experiments, we used a mixture of monocyclic terpenes, obtained by distillation of the products

*Carried out with the participation of O. F. Gorbunova and students K. E. Sosnina and V. I. Lisov.

of isomerizing α-pinene over titanic acid and consisting of dipentene, α-terpinene and terpinolene: the b. p. was 177-185° at 763 mm and the product had $n^{20}D$ 1.4810, d^{20}_4 0.854.

The irreversible catalysis was carried out by the procedure and in the apparatus described previously [1].

Into the reactor was placed a mixture of terpenes, measured by pipette; then the catalyst was introduced as a paste with a tared iron spoon and after this, the reactor was placed on a sand bath, preliminarily heated to 250°. In all experiments, the moment when the liquid in the reactor reached 150° was taken as the beginning of the reaction. The reaction rate was determined by measurements of the "bromine numbers" of the catalyzates during the course of experiments by titration of samples of the catalyzates with an alcohol solution of 0.5 N bromide-bromate mixture in the presence of hydrochloric acid [8].

The rate of catalysis was expressed as "degree of conversion", x per unit time. The specific gravities of the catalyzates and the starting mixtures of terpenes were very close to each other (they could be considered practically identical) and then x was determined by the formula

$$x = \left(1 - \frac{a}{b}\right) \cdot 100\%,$$

where a is the number of milliliters of 0.5 N solution of bromide-bromate mixture consumed in titration of 0.5 ml of catalyzate and b the same for titration of 0.5 ml of the original mixture of terpenes.

So that comparable results were obtained, all experiments were carried out with the same sample of catalyst and the same mixture of terpenes, which had to be freshly distilled.

Experiment 1. A) 16 g of the terpene mixture and 0.3 g of fresh catalyst paste were used. Half an hour after the beginning of the experiment, the dgree of conversion of the mixture reached 99%.

b) The mixture was allowed to settle, the catalyzate decanted from the reactor, and to the residual catalyst was added a fresh portion (16 g) of terpenes. After 1 hour, the degree of conversion reached only 2.3%.

c) The spent catalyst (0.3 g) was washed several times in the reactor with an alcohol-benzene mixture under conditions which excluded the possibilility of contact with air. After careful decantation of the solvent, 16 g of the mixture of terpenes was added to the catalyst.

After 1 hour the degree of conversion was 2.3%.

Experiment 2. a) 16 g of the terpene mixture and 0.3 g of fresh catalyst was used. After half an hour the degree of conversion was 99%.

b) A portion of fresh catalyst paste was placed in a porcelain dish and dried in a drying cupboard at 105°; 16 g of terpene mixture and 0.3 g of this catalyst was taken. After 3 hours, the degree of conversion was only 4%.

c) The dried catalyst was placed in a quartz tube and heated for 2 hours in a stream of hydrogen at 350°. With the hydrogen stream still flowing, the catalyst was poured into the reactor containing 16 g of the terpene mixture. After 2 hours the degree of conversion was 76.2% and after 2 hours 40 minutes, 79.5%.

Experiment 3. 0.68g of spent catalyst, which had completely lost its activity, was washed with alcohol and introduced into a "duck"• containing 50 ml of alcohol. The "duck" was connected to a burette with hydrogen and shaken for 3.5 hours at room temperature, when 20 ml of hydrogen was absorbed. For catalysis we used 0.3 g of catalyst, taken directly from the "duck", and 16 g of the terpene mixture. After 2 hours 20 minutes, the degree of conversion reached 87% and after 3 hours 40 minutes, 97%; the reaction was then stopped.

Experiment 4. Catalyst from the previous experiment was introduced into a "duck" and treated with hydrogen for 3 hours, as in the previous experiment. 16 ml of hydrogen was absorbed. The catalyst was then introduced into the reactor under a layer of alcohol, the alcohol decanted, 16 g of the terpene mixture added and catalysis carried out. After 2 hours 20 minutes, the degree of conversion was 79%.

Experiment 5. a) 2.6 g of fresh catalyst was placed in a "duck" with 25 ml of dioxane, connected to the hydrogen source and shaken for 20 minutes. 6 ml of hydrogen was absorbed. With 0.3 g of such a catalyst,

• "Duck" is a literal translation of the Russian work "utka," which is the Russian term for a longnecked hydrogenation flask. (Publishers note).

taken from the "duck", the catalysis of 16 g of the terpene mixture was practically complete after 0.5 hours.

b) To the catalyst, remaining in the "duck" under a layer of dioxane, was added 5.37 g of Michler's ketone and after the hydrogen had been flushed from the "duck" with nitrogen, the contents were shaken in a nitrogen atmosphere for 1 hour at 50° (the nitrogen we used did not have any effect on the activity of fresh catalyst).

We took 0.3 g of catalyst, treated with Michler's ketone, and 13 g of the terpene mixture; after 35 minutes, the degree of conversion reached 58% and after 2.5 hours, 68%, when the reaction stopped.

c) The catalyst remaining in the "duck" was shaken for a further 4 hours. For catalysis we used 16 g of terpenes and 0.3 g of catalyst; after 35 minutes, the degree of conversion was 42%, after an hour, 50%, after 3 hours 10 minutes, 68% and then the reaction stopped.

d) The catalyst remaining in the "duck", after decantation of the dioxane solution of Michler's ketone and repeated washing with dioxane, was shaken in the "duck" with 25 ml of freshly distilled nitrobenzene for 1 hour in a nitrogen atmosphere.

After this treatment, the catalyst was inactive in irreversible catalysis.

Experiment 6. 0.7 g of fresh catalyst and 25 ml of nitrobenzene were shaken in a "duck" in a nitrogen atmosphere for 2 hours, the nitrobenzene decanted and the catalyst washed with alcohol several times in the absence of air. After such treatment, the catalyst lost its activity.

Experiment 7. a) A freshly distilled mixture of terpenes was left for 7 days in a flask closed with a cork. A test for peroxides with potassium iodide in the presence of starch indicated a considerable amount of peroxide compounds. For catalysis we used 16 g of such a mixture of terpenes and 0.3 g of catalyst. After 1 hour the degree of conversion was 40%.

b) After steam distillation or treatment with an aqueous solution of ferrous sulfate, the oxidized mixture of terpenes underwent irreversible catalysis normally, as in experiment 1, a).

SUMMARY

1. The activity of Raney nickel as a catalyst in N. D. Zelinskii irreversible catalysis is caused by the presence of hydrogen in the catalyst. Dehydrogenation of the catalyst leads to its deactivation: removal of adsorbed hydrogen considerably lowers its activity and removal of adsorbed and dissolved hydrogen completely deactivates the catalyst.

2. The activity of the catalyst is restored after its treatment with hydrogen.

3. Peroxides present in the substance strongly deactivate the catalyst.

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** In Russian.

INVESTIGATION OF THE INTERACTION OF BENZIDINE WITH ORGANIC ACIDS

A. P. Arestenko and A. G. Bergman

Kuban Agricultural Institute

The object of the present investigation was to establish the character of the interaction of amino compounds with oxygen-containing organic substances. The example studied was the binary systems of benzidine with organic acids. The visual polythermal method was used for constructing the melting point curves. The temperatures were determined with an accuracy of ± 0.5°. The components were melted in a tube placed in a glass glycerol sleeve. The melts were stirred vigorously with a glass stirrer and seeds introduced. Purified substances with constants close to those reported in the literature were used. The compositions of the mixtures were calculated in molecular percents. The numerical data are presented in the table.

1. Benzidine – acetic acid system (Fig. 1). The acetic acid we used had m. p. 16° and $n^{25}D$ 1.3711. In the system there was formed a compound at 105° having a 1 : 1 composition, i.e., $(C_6H_4)_2(NH_2)_2 \cdot CH_3COOH$, which readily dissociated in melts with eutectics at 12° and 5%, and 101° and 62% of benzidine. The solutions had a high viscosity and began to decompose when heated to slightly above the liquidus curve. Since the boiling point of acetic acid lies below the melting point of benzidine, the branch of the melting point curve on the benzidine side was determined approximately.

2. Benzidine – propionic acid system (Fig. 1). It can be proposed that in the system there is formed an equimolecular, readily decomposable compound with a 1 : 1 composition, i.e., $(C_6H_4)_2(NH_2)_2 \cdot CH_3CH_2COOH$ with a transition point at 52° and 29% benzidine and a eutectic at -24° and 5% benzidine.

3. Benzidine – n-butyric acid system (Fig. 1). Various values are reported in the literature for the melting point of n-butyric acid, namely -3.1, -4.7 and -7.9°. We found m. p. -7.9° and $n^{20}D$ 1.3979. The system forms an unstable compound, probably with a 1 : 1 composition, i.e., $(C_6H_4)_2(NH_2)_2 \cdot CH_3(CH_2)_2COOH$, with a transition point at 52° and 26% and a eutectic at -11° and 2.5% benzidine.

4. Benzidine – isobutyric acid system (Fig. 1). Here also there is formed only one readily decomposable compound with a 1 : 1 composition, i.e., $(C_6H_4)_2(NH_2)_2 \cdot (CH_3)_2CHCOOH$, with a transition point at 52° and 24% of benzidine.

The points on the curve of the 1 : 1 compound, which is a dotted one, were determined on separate samples due to decomposition of the melt. We did not detect a eutectic due to supercooling of the melt.

The isobutyric acid used had m. p. -47° and $n^{20}D$ 1.3930.

5. Benzidine – isovaleric acid system (Fig. 1). A eutectic was not detected due to supercooling. The components form one dissociating compound, probably with a 1 :1 composition, i. e., $(C_6H_4)_2(NH_2)_2 \cdot (CH_3)_2CHCH_2COOH$. The transition point lies at 67° and 18% of benzidine.

6. Benzidene – n-caprylic acid system (Fig. 1). The components form a readily dissociable compound, apparently with a 1 : 1 composition, i.e., $(C_6H_4)_2(NH_2)_2 \cdot CH_3(CH_2)_6COOH$. The transition point lies at 52° and 13% and the eutectic at 15.5° and 0.1% of benzidine.

7. Benzidine – stearic acid system (Fig. 1). Compounds were not formed and the liquid phase separated into layers from 10 to 75% of stearic acid.

Binary Systems of Benzidine with Organic Acids *

CH_3COOH (mole %)	Temp.	CH_3CH_2COOH (mole %)	Temp.	$CH_3(CH_2)_2COOH$ (mole %)	Temp.	$(CH_3)_2CHCOOH$ (mole %)	Temp.	$(CH_3)_2CHCH_2COOH$ (mole %)	Temp.	$CH_3(CH_2)_3COOH$ (mole %)	Temp.	C_6H_5COOH (mole %)	Temp.	$C_6H_4(OH)COOH$ (mole %)	Temp.	o-HOC_6H_4COOH (mole %)	Temp.
0	128.0°	0	128.0°	0	128.0°	0	128.0°	0	128.0°	0	128.0°	0	128.0°	0	128.0°	0	128.0°
12	122.0	10	125.0	10	123.0	10	126.0	10	124.0	10	123.0	1	127.0	10	122.0	5	125.0
20	117.0	20	119.0	20	116.0	20	120.0	20	118.0	20	115.0	3	126.0	20	114.0	10	122.0
30	111.0	30	112.0	30	110.0	30	114.0	30	113.0	30	110.0	5	125.0	25	110.0	15	119.0
37	101.5	40	102.0	40	103.0	40	102.0	40	107.0	50	104.0	10	125.0	30	114.0	20	120.0
41	102.0	50	91.0	50	93.0	50	95.0	50	101.0	60	98.0	20	125.0	35	101.0	25	126.0
50	105.0	60	78.0	60	83.0	60	83.5	65	91.0	70	93.5	30	125.0	40	100.0	35	138.0
60	103.0	65	68.0	65	78.0	70	65.5	75	82.0	80	85.0	40	125.0	44	102.0	45	149.0
65	102.0	70	57.0	72	67.0	75	55.0	78	76.0	83	80.0	50	125.0	50	103.0	50	152.0
70	98.0	71	52.0	73	62.0	78	53.0	79	73.0	85	73.0	60	124.0	55	103.0	55	156.0
80	86.0	73	51.0	74	53.0	81	54.0	80	71.0	87	52.0	70	122.0	60	104.0	60	159.0
90	61.0	75	50.0	75	52.0	85	55.0	81	67.0	90	51.0	80	114.0	65	107.0	65	161.0
93	45.0	80	47.0	80	50.0	90	50.0	85	68.0	95	44.0	85	103.0	70	108.0	70	160.5
95	12.0	85	41.0	85	45.0	93	46.0	90	64.0	98.5	32.0	90	94.0	75	109.0	75	158.0
97	14.0	90	25.0	90	36.0	96	37.0	95	57.0	99.2	27.0	95	82.0	80	108.0	80	152.0
100	16.0	92	17.0	93	22.0	100	—47.0	98	43.0	99.9	16.0	97	77.0	85	112.0	85	147.0
		95	—24.0	95	9.0			100	—37.5	100	16.0	98.5	69.0	90	114.5	90	150.0
		97	—23.0	98	—10.0							100	69.0	95	118.0	95	154.0
		100	—22.0	100	—7.9									100	121.7	100	157.0

* The number of experimental points has been reduced.

8. Benzidine – benzoic acid system (Fig. 2). Two readily dissociating compounds are formed with 1 : 1 and 1 : 3 composition, i. e., $(C_6H_4)_2(NH_2)_2 \cdot C_6H_5COOH$ and $(C_6H_4)_2(NH_2)_2 \cdot 3C_6H_5COOH$, with m. p. 103 and 109°. There are eutectics at 99° and 62%, and 108° and 20% of benzidine. The transition point corresponds to 104° and 40% of benzidine.

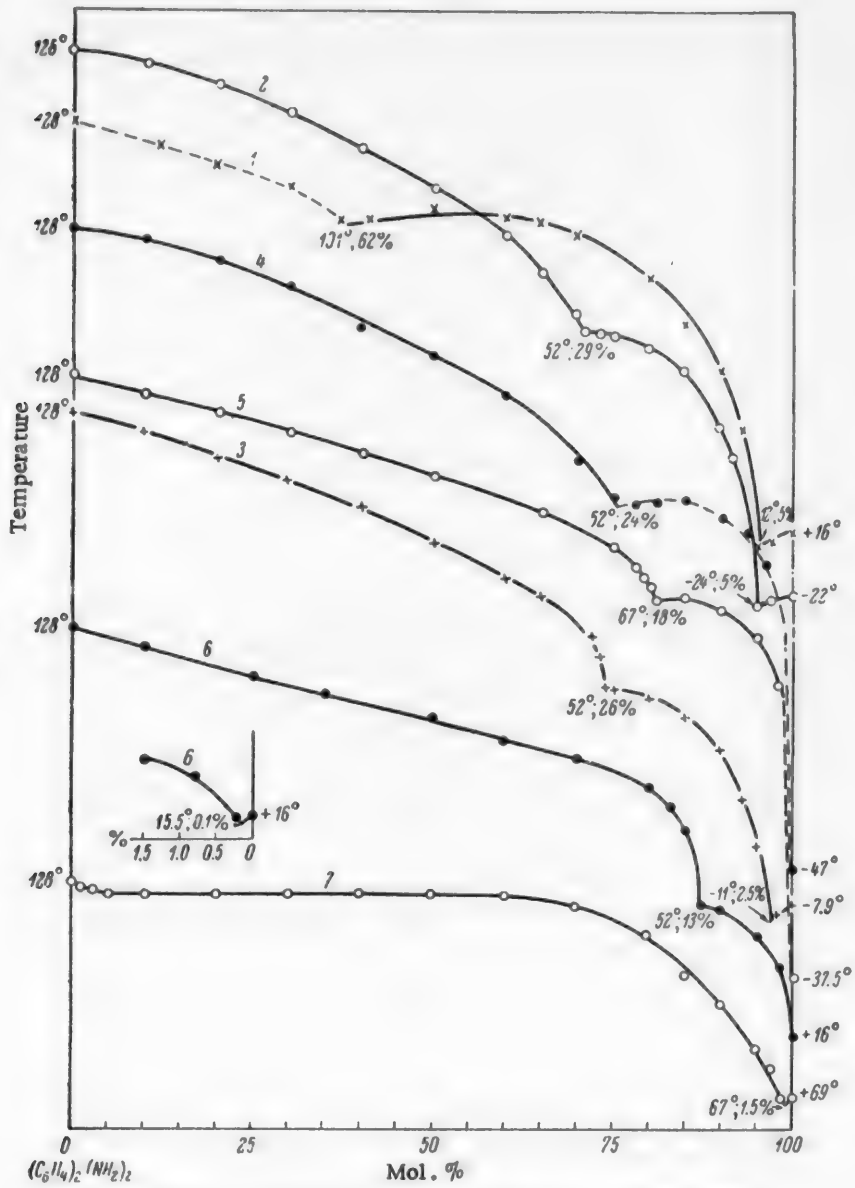


Fig. 1. Melting point diagrams of binary systems. 1) $(C_6H_4)_2(NH_2)_2$ – $-CH_3COOH$, 2) $(C_6H_4)_2(NH_2)_2$ – CH_3CH_2COOH, 3) $(C_6H_4)_2(NH_2)_2$ – $-CH_3CH_2CH_2COOH$, 4) $(C_6H_4)_2(NH_2)_2$ – $(CH_3)_2CHCOOH$, 5) $(C_6H_4)_2(NH_2)$– $-(CH_3)_2CHCH_2COOH$, 6) $(C_6H_4)_2(NH_2)_2$ – $CH_3(CH_2)_6COOH$, 7) $(C_6H_4)_2(NH_2)_2$ – $-C_{17}H_{35}COOH$.

On gentle heating, the melts changed from a tobacco color to a dark green; in all probability there was partial decomposition here and due to this, the melting point curve could not be determined with the necessary accuracy.

9. Benzidine – salicylic acid system (Fig. 2). A dissociating compound is formed with a 1 : 2 composition, i. e., $(C_6H_4)_2(NH_2)_2 \cdot 2$ o-HOC_6H_4COOH, and this melts at 161° and there are eutectics at 117° and 82% and 146° and 15% of benzidine. With very slight overheating, the mixtures changed color in the following way: on the benzidine side, up to 20% salicylic acid, they changed to green, from 20 to 35%, to dark green and from 35 to 80% of salicylic acid, to a bright blue. The gas evolution observed indicates decomposition of the components.

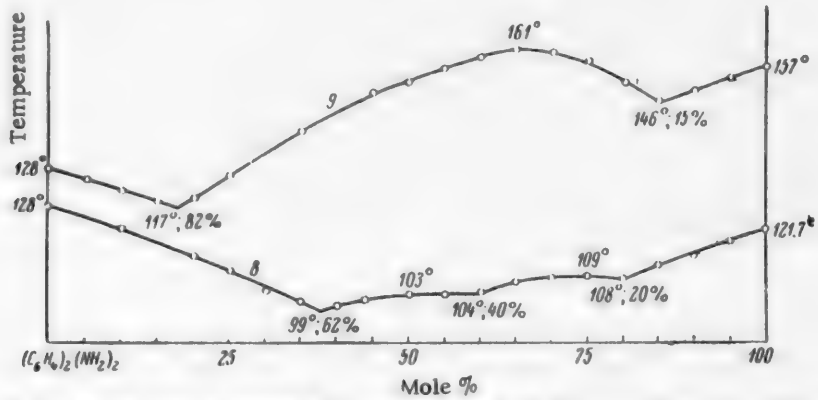


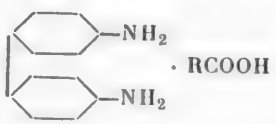
Fig. 2. Melting point diagrams of binary systems. 8) $(C_6H_4)_2(NH_2)_2$ – C_6H_5COOH, 9) $(C_6H_4)_2(NH_2)_2$ – HOC_6H_4COOH.

DISCUSSION OF RESULTS

Investigation of the interaction of acids with benzidine involves a series of difficulties caused by the instability of benzidine in mixtures with acids, especially when heated above the melting point curve. In exactly the same way, prolonged heating at lower temperatures produces continuous, gradual decomposition, often accompanied by the appearance of a characteristic color which is particularly noticeable with salicylic acid.

It might be expected that the two separate amino groups of benzidine would react independently of each other, forming both 1 : 1 and 1 : 2 compounds, and then, in addition, would form acid salts with 1 : 3 and 1 : 4 composition and also basic salts with 2 : 1, 2 : 2, and 3 : 2 composition.

Finally, there is the possibility of conjugated participation of both amino groups with one amino group bound to the acid molecule and the second amino group connected to it with a hydrogen bond to form a type of internal complex.



Such compounds of a simple nature are known to us, for example $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$.

Therefore the absence of compounds of benzidine with other aliphatic monobasic acids of the 1 : 2 type may only be explained by the addition of the second amino group to the ammonium salt, formed at the other end of the molecule.

The possibility of such an explanation must be confirmed by x-ray structural analysis. Finally, we cannot exclude the possibility of the addition of a benzidine molecule to another molecule which has already added two acid molecules.

As we showed previously [1], with benzidine, phenol forms a compound with a 2 : 1 composition. In this case it may be supposed that in the benzidine – phenol system two phenol groups are added to both amino

groups of benzidine; however, with this supposition, the absence of a 1 : 1 compound with phenol is not explained. The latter phenomenon is reminiscent of the interaction of ethylenediamine with monohydric alcohols from methyl to benzyl; in all systems only the compounds of one molecule of ethylenediamine with two molecules of the monohydric alcohols are formed [2, 3]. There are no compounds of ethylenediamine with one molecule of alcohol, although with water ethylenediamine forms both 1 : 1 and 1 : 2 compounds. The work of A. G. Bergman and Z. A. Koloskova [4] showed that ethylenediamine gives compounds with a 1 : 4 composition with monobasic aliphatic acids.

Salicylic acid forms only a 1 : 2 compound and not a 1 : 1 compound, although it seems that there is the possibility of combination of the one amino group of benzidine with the acid group and the other amino group with the phenolic hydroxyl.

SUMMARY

1. Binary systems of benzidine with organic acids were studied through the melting point diagrams. The liquidus curves reflected the formation of readily dissociable compounds of the probable composition:

1. $(C_6H_4)_2(NH_2)_2 \cdot CH_3COOH$;
2. $(C_6H_4)_2(NH_2)_2 \cdot CH_3CH_2COOH$;
3. $(C_6H_4)_2(NH_2)_2 \cdot CH_3(CH_2)_2COOH$;
4. $(C_6H_4)_2(NH_2)_2 \cdot (CH_3)_2CHCOOH$;
5. $(C_6H_4)_2(NH_2)_2 \cdot (CH_3)_2CHCH_2COOH$;
6. $(C_6H_4)_2(NH_2)_2 \cdot CH_3(CH_2)_6COOH$;
7. $(C_6H_4)_2(NH_2)_2 \cdot C_6H_5COOH$ and $(C_6H_4)_2(NH_2)_2 \cdot 3C_6H_5COOH$;
8. $(C_6H_4)_2(NH_2)_2 \cdot 2HOC_6H_4COOH$.

Apparently, compounds of other compositions are not formed.

2. Separation into layers was observed in the benzidine – stearic acid system in the range from 10 to 90% of acid. There was no complex formation in this system.

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INTERACTION OF DIAZOACETIC ESTER WITH ACETYLENIC HYDROCARBONS

I. A. D'yakonov and M. I. Komendantov

Leningrad State University

In 1956 we published a short communication [1] on a new reaction of diazoacetic ester (ethyl) with an acetylenic hydrocarbon, 1-phenylpropyne. As a result of our experiments, we obtained a previously undescribed ester of 3-methyl-2-phenylcyclopropenecarboxylic acid. Since we were unable to establish the position of the double bond in the ring completely, the investigation was continued. It was found that the physical constants of the compound given in the communication [1] were not quite accurate. The corrected constants are given below.

B. p. 97-101° at 0.2 mm, d^{20}_4 1.08001, $n^{20}D$ 1.57732, MR_D 62.08; calc. 58.32.

The infrared and ultraviolet spectra remained almost unchanged.

To establish the structure conclusively, it was necessary to synthesize esters of other cyclopropenecarboxylic acids. For this purpose, we reacted diazoacetic ester with tolane and obtained a new cyclopropene derivative. When the structure of this was established, we again returned to the investigation of the first of the derivatives obtained and at the end of this work we propose to give a complete account of its results. The present letter to the editor is connected with the fact that at the end of 1958 a short communication by American chemists [2] appeared in which their work diazoacetic ester on the tolane formed a condensation product, whose hydrolysis led to 2,3-diphenyl-Δ2-cyclopropene-1-carboxylic acid (Ia). The note gave no information on the conditions for the preparation of acid (Ia). The data we obtained as a result of investigation of the same reaction differ from the data of Breslow and Battiste [2]. It is possible that the reason for this difference is different conditions for isolating the final reaction products. The results of our observations are presented below.

In the reaction we used 0.5 mole of tolane and 0.5 mole of diazoacetic ester, the catalyst was anhydrous copper sulfate and the solvent was cyclohexane (0.5 mole). The reaction was carried out in an atmosphere of pure nitrogen. The condensation product was fractionated in high vacuum.

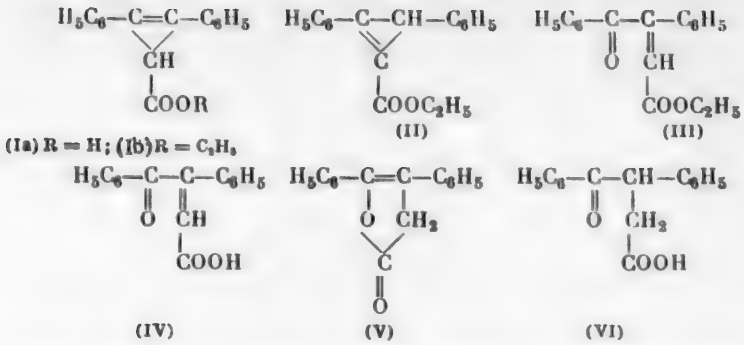
B. p. 138-142° (0.3 mm), m. p. 38-39° (from methanol).

Found %: C 81.64; H 6.25; OC_2H_5 17.06. $C_{13}H_{16}O_2$. Calculated %: C 81.79; H 6.10; OC_2H_5 17.04.

The infrared spectrum (of a melt) showed strong absorptions at 5.80, 6.31, 7.20, 7.63, 8.26, 8.48, 9.57, 9.77, 11.09 μ. The ultraviolet spectrum (in 0.003 M hexane showed λ_{max} 308 μ, ϵ_{max} 24000.

Oxidation of the substance with lead tetraacetate in dry benzene and also treatment of this compound in ether solution with dry oxygen formed ester (III); the yield were 93 and 73%, respectively. Heating the condensation product with water in the presence of hydrohalic or acetic acids yielded lactone (V); the yield was 92%. Alkaline hydrolysis of (III) and (V) yielded acid (IV) and (VI), respectively. The yields of (IV) and (VI) were 89 and 94.3%. (IV), (V) and (VI) were identified by mixed melting points with authentic preparations.

Data from chemical and spectral investigations of the condensation product indicated that it had the structure (II) rather than (Ib).



(Ia) R = H; (Ib) R = C_2H_5

(II) (III)

(IV) (V) (VI)

Ozonization of (II) and subsequent decomposition of the ozonization product with water yielded decylene-acetic acid and a small amount of benzil; dibenzoylmethane, which was found in the oxidation products of (Ia) [2], was not detected. Attempts to obtain the corresponding acid from ester (II) have been unsuccessful up to now.

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STUDY OF THE MECHANISM OF ACID-BASE INTERACTION BY DEUTERIUM EXCHANGE

A. I. Shatenshtein and E. N. Zvyagintseva

L. Ya. Karpov Physicochemical Institute

The double reactivity of aromatic amines is caused by p, π-conjugation (A. N. Nesmeyanov) and is reflected in their reactions with acids, not only at the N atom, but also at the ortho and para atoms of the ring. The latter reaction produces hydrogen exchange. The addition of H^+ to the electron pair of the nitrogen disrupts the conjugation and must hinder exchange. According to Bronsted's scheme, in acid-base interaction the valence state of the nitrogen does not depend on the nature of the acid and therefore, in the reactions of dimethylaniline with different acids, the effect should be the same. If on increasing the strength of the acid and also its dielectric constant (DC), the exchange rate falls, it means that the extent to which the nitrogen is ionized increases and, consequently, that Bronsted's scheme does not describe the interaction mechanism completely. Triphenylamine is such a weak base that it does not give a salt with HBr and, as is normal for acid exchange, its rates will increase with the strength of the acid. Methyldiphenylamine only reacts with the strongest carboxylic acids and therefore, if the Bronsted scheme is not exact, on increasing the strength of the acid, the exchange reaction rate will pass through a maximum.

The results of experiments, carried out with a large excess of anhydrous CH_3COOH, HCOOH, $CH_2ClCOOH$, CCl_3COOH and CF_3COOH and amines, in which the ortho and para H atoms were replaced by D, indicate the inadequacy of the Bronsted scheme in accordance with other facts [1]. The rate constants (sec^{-1}) were determined approximately, but by the conditions of the experiments, this cannot affect their order.

Further work is being aimed at raising the accuracy of the results.

Amine	CH_3COOH (DC $_{25°}$ 6.2)	HCOOH (DC $_{16°}$ 58.5)	$CH_2ClCOOH$ (DC $_{80°}$ 12)	CCl_3COOH (DC $_{81°}$ 4.5)	CF_3COOH (DC $_{25°}$ 8.1)	HBr [2] (DC $_{25°}$ 3.8)
$C_6H_2D_3N(CH_3)_2$	10^{-4} (90°)	10^{-5} (90°)	$5\cdot10^{-5}$ (90°)	10^{-5} (90°)	$5\cdot10^{-6}$ (90°)	$< 10^{-8}$ (20°)
$(C_6H_2D_3)_2NCH_3$	10^{-5} (90°)	10^{-3} (90°)	10^{-3} (65°)	10^{-3} (65°)	10^{-4} (65°)	—
$(C_6H_2D_3)_3N$	10^{-7} (90°)	10^{-4} (90°)	10^{-4} (90°)	—	10^{-3} (30°)	$> 10^{-2}$ (20°)

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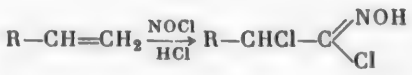
PREPARATION OF ACID CHLORIDES OF α-CHLOROISOBUTYRO- AND α-CHLORO-α-METHYLBUTYROHYDROXAMIC ACIDS FROM 2-METHYLPROPENE AND 2-METHYLBUTENE-1

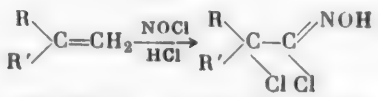
K. A. Ogloblin

Leningrad State University

In one of our previous communications* it was shown that monosubstituted ethylenic hydrocarbons react with nitrosyl chloride in ether solution in the presence of hydrogen chloride to give acid chlorides of α-chloro substituted hydroxamic acids.



At the present time we have found that under analogous conditions unsymmetrical disubstituted ethylenic hydrocarbons, 2-methylpropene and 2-methylbutene-1, also form acid chlorides of α-chloro substituted hydroxamic acids, namely α-chloroisobutyrohydroxamic (I) and α-chloro-α-methylbutyrohydroxamic (II) acids, in yields of about 40%.



R=R′=CH₃ (I); R=CH₃, R′=C₂H₅ (II).

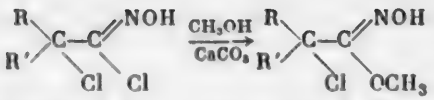
Thus, the new method of preparing acid chlorides of α-chloro substituted hydroxamic acids, discovered for monosubstituted ethylenic hydrocarbons, has also been extended to unsymmetrical disubstituted ethylenic hydrocarbons.

The properties of compounds (I) and (II), which were obtained, are presented in the table.

Compounds (I) and (II) were viscous, colorless liquids, which rapidly became turbid in air and had a specific smell. They were hydrolyzed by water, even in the cold, and an aqueous solution gave a reaction for hydroxamic acid (a red-violet color with a ferric chloride solution). Hydrolysis of (I) and (II) yielded, respectively, α-hydroxyisobutyric acid and α-chloromethylethylacetic acids and also hydroxylamine hydrochloride.

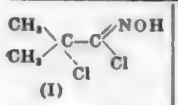
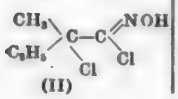
Heating (I) and (II) with methyl alcohol in the presence of marble formed the methyl esters of α-chloroisobutyrohydroxamic (III) (m. p. 103-103.5°) and α-chloro-α-methylbutyrohydroxamic (IV) (m. p. 85-85.5°) acids, respectively.

* See J. Gen. Chem. 29, 264 (1959).



R=R'=CH_3 (III); R=CH_3, R'=C_2H_5 (IV).

In the experiment with isobutylene, together with the main product (I), we also obtained small amounts of 3-chloro-2-methylpropene-1 (b. p. 69-73°, d_4^{20} 0.9227, $n^{20}D$ 1.4247) and 1,2-dichloro-2-methylpropane (b. p. 102°, d_4^{20} 1.0679, n_D^{20} 1.4324).

Formula	Boiling point at 3 mm	d_4^{20}	n_D^{20}	MR_D		Cl(%)	
				found	calc.	found	calc.
 (I)	64—65°	1.2843	1.4910	35.19	35.10	45.17	45.50
 (II)	73—74	1.2526	14920	39.38	39.35	41.31	41.70

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THE APPLICABILITY OF A. F. KAPUSTINSKII'S EQUATION FOR CALCULATING THE ENERGY OF THE CRYSTAL LATTICE OF COMPLEX SALTS

S. N. Andreev, E. V. Stroganov, and V. G. Khaldin

Leningrad State University

Calculation of the heats of formation of complex ions and the heats of addition of addends to ion-complex-formers and also the calculation of the heats of solvation of ions are only possible when lattice energy values of the complex salt crystals are known.

Experimental determination of crystal lattice energies is extremely complex and, as a result of this, these values have only been determined experimentally for a very small number of substances with crystal lattices, composed of the simplest ions.

On the basis of the Born – Lande [1] and Born – Mayer [2] equations, A. F. Kapustinskii [3-5] deduced an equation for the energy of an ionic crystal lattice, which made it possible to calculate this value from the Goldschmidt values of the radii of the ions forming the crystalline lattice of the chemical compound.

In the case of alkali and alkaline earth metal halides and also for a series of other binary compounds of ionic structure, the numerical values of the crystal lattice energies, found by calculation from A. F. Kapustinskii's equation, agree well with the values found experimentally [3-5].

K. B. Yatsimirskii proposed that A. F. Kapustinskii's equation was also applicable to the calculation of crystal lattice energies of complex salts. Here he considered two cases.

1) When the complex ion has the form of a right octahedron or a right tetrahedron. In this case the crystal lattice energy of the salt may be calculated by putting the crystallochemical radius of the complex ion into A. F. Kapustinskii's equation.

2) When the ion differs in form from a right octahedron or tetrahedron. In this case the crystal lattice energy of the complex compound may be found by putting into this equation the "thermochemical" radius of the ion.

Though the second premise can hardly be disputed, since the thermochemical radius of an ion is taken as "the radius of a hypothetical spherical ion, isoenergetically replacing the given ion in the crystal lattice of the salt" [6, 7], the first premise, accepted by K. B. Yatsimirskii without proof, requires discussion.

First of all, the problem arises as to whether it is possible to approximate a polyatomic complex ion to a sphere with a uniform charge distribution on its surface and whether the radius of this sphere will coincide with the crystallochemical radius of this ion, determined from x-ray structural data.

In addition, since A. F. Kapustinskii's equation does not allow for van der Waals forces acting between ions in the crystal lattice of the salt, this equation is to some extent approximate. By calculation, Mayer and Helmholz [8] showed that in the case of crystal lattices consisting of the simplest ions, the van der Waals interaction of the ions was hardly reflected in the crystal lattice energy.

Similar calculations have not been carried out for the crystal lattices of complex salts, which also raises

doubts on whether, when the crystallochemical radii of complex octahedral or tetrahedral ions are introduced into A. F. Kapustinskii's equation, the latter gives a sufficiently accurate value for the crystal lattice energy of the complex salt.

In connection with what has been said, it was necessary to test the applicability of A. F. Kapustinskii's equation and the applicability of the accepted "crystallochemical radius" for calculating the crystal lattice energies of salts with complex ions of octahedral and tetrahedral configurations.

In solving the problem of the possibility of applying the accepted "crystallochemical radius" to complex ions, it is possible to proceed by the method accepted for the simplest ions, i. e. , by taking a series of crystalline structures formed by the same complex ion with various simple ions of opposite charge to calculate the interionic distances. If the difference between this distance and the Goldschmidt radius of the second ion varies only to an insignificant extent when the chemical nature of the second ion is changed, then this value can be considered as the crystallochemical radius of the complex ion.

To solve the problem of the possibility of applying A. F. Kapustinskii's equation to the calculation of the crystal lattice energies of salts with complex ions of octahedral or tetrahedral configuration, we used the method of differences [6 7]. The use of this method for solving the given problem may be illustrated by the following example. Let us assume that we have the complex slats $[MX_6]A$ and $[MX_6]B$, containing the same complex ion $[MX_6]$ but different ions A and B, where the crystallochemical radii of these ions, r_A and r_B , are known.

If the experimental values of the heats of formation of these salts, ΔH_{KA} and ΔH_{KB} are known, and likewise the heats of formation of the ions of A and B in the gas phase, ΔH_A and ΔH_B, then expressing ΔH_{KA} and ΔH_{KB} in terms of the heats of formation of the ions and the crystal lattice energy, U, we obtain:

$$\Delta H_{KA} = \Delta H_K + \Delta H_A - U_{KA},$$

$$\Delta H_{KB} = \Delta H_K + \Delta H_B - U_{KB}.$$

In order to remove the value ΔH_K, i.e., the heat of formation of the complex ion, from the consideration, we take the difference of these equations:

$$(\Delta H_{KA} - \Delta H_{KB}) - (\Delta H_A - \Delta H_B) = U_{KB} - U_{KA}$$

Replacing U_{KB} and U_{KA} by their values calculated by A. F. Kapustinskii's equation [5], we arrive at the equality:

$$(\Delta H_{KA} - \Delta H_{KB}) - (\Delta H_A - \Delta H_B) = 287.2 \frac{Z_K \cdot Z_B \sum n}{r_K + r_B} \left[1 - \frac{0.345}{r_K + r_B} + 0.00435 (r_K + r_B) \right] - 287.2 \frac{Z_K \cdot Z_A \sum n}{r_K + r_A} \left[1 - \frac{0.345}{r_K + r_A} + 0.00435 (r_K + r_A) \right] \quad (1)$$

The only unknown in this equation is the value r_K.

If the approximation of the ion to a sphere is possible and the van der Waals forces in the complex salts we are considering are as small as in salts formed by simple ions, then A. F. Kapustinskii's equation must give accurately the value of the crystal lattice energy of the complex salt.

In this case, solving equation (1) for r_K, we must obtain a value which differs little from the value of the crystallochemical radius of the complex ion.

If, for the reasons considered previously, A. F. Kapustinskii's equation does not accurately represent the crystal lattice energies of the complex salts, then solving equation (1) for r_K we obtain some coefficient, which has nothing in common with the crystallochemical radius of the complex ion, calculated from x-ray data.

We carried out work on determining the crystallochemical radii of complex ions of octahedral and tetrahedral configuration, and also tests of the applicability of A. F. Kapustinskii's equation for calculating the crystal lattice energy of complex salts by the method of differences on a comparatively small number of chemical compounds. The reason for this is the difficulty of choosing complex compounds for which both the crystal structures are known and the heats of formation have been determined with sufficient reliability.

We obtained data on the heats of formation of complex salts and also data on the heats of formation of ions in the gas phase from the summary of Rossini, Evans et al. [9].

Ion	The crystallochemical radius of the ion was calculated from the structure of the compound	Values of ionic radii (in A°)		
		calc. from x-ray struc. analysis data	average values	calc. from thermochemical data
$Mg(NH_3)_6^{+2}$	$Mg(NH_3)_6Cl_2$ $Mg(NH_3)_6Br_2$ $Mg(NH_3)_6I_2$ $Mg(NH_3)_6(ClO_4)_2$	2.58 2.58 2.55 2.63	2.59	2.59 ± 0.20
$Zn(NH_3)_6^{+2}$	$Zn(NH_3)_6I_2$ $Zn(NH_3)_6(ClO_4)_2$	2.55 2.64	2.60	2.70 ± 0.15
$Cd(NH_3)_6^{+2}$	$Cd(NH_3)_6I_2$ $Cd(NH_3)_6(ClO_4)_2$	2.58 2.66	2.62	2.71 ± 0.08
$Mn(NH_3)_6^{+2}$	$Mn(NH_3)_6Cl_2$ $Mn(NH_3)_6Br_2$ $Mn(NH_3)_6I_2$ $Mn(NH_3)_6(ClO_4)_2$	2.61 2.59 2.59 2.65	2.61	2.63 ± 0.15
$Fe(NH_3)_6^{+2}$	$Fe(NH_3)_6Cl_2$ $Fe(NH_3)_6Br_2$ $Fe(NH_3)_6I_2$ $Fe(NH_3)_6(ClO_4)_2$	2.61 2.59 2.59 2.65	2.61	2.59 ± 0.23
$Co(NH_3)_6^{+2}$	$Co(NH_3)_6Cl_2$ $Co(NH_3)_6Br_2$ $Co(NH_3)_6I_2$ $Co(NH_3)_6(ClO_4)_2$	2.55 2.54 2.55 2.60	2.57	2.62 ± 0.14
$Ni(NH_3)_6^{+2}$	$Ni(NH_3)_6Cl_2$ $Ni(NH_3)_6Br_2$ $Ni(NH_3)_6I_2$ $Ni(NH_3)_6(ClO_4)_2$	2.54 2.53 2.51 2.58	2.54	2.66 ± 0.3
$Cu(NH_3)_4^{+2}$	$Cu(NH_3)_4Br_2$ $Cu(NH_3)_4I_2$	2.50 2.44	2.47	2.63
$Mg(H_2O)_6^{+2}$	$Mg(H_2O)_6(ClO_4)_2$	2.31	2.31	2.26
$Zn(H_2O)_6^{+2}$	$Zn(H_2O)_6(ClO_4)_2$	2.30	2.30	2.35 [11]
$Mn(H_2O)_6^{+2}$	$Mn(H_2O)_6(ClO_4)_2$	2.36	2.36	2.35 [11]
$Co(H_2O)_6^{+2}$	$Co(H_2O)_6(ClO_4)_2$	2.30	2.30	2.34 [11]
$Ni(H_2O)_6^{+2}$	$Ni(H_2O)_6(ClO_4)_2$	2.29	2.29	2.29 [11]
$PtCl_6^{-2}$	K_2PtCl_6 Rb_2PtCl_6 Cs_2PtCl_6 Tl_2PtCl_6	2.88 2.79 2.76 2.73	2.80	2.98
SiF_6^{-2}	K_2SiF_6 Rb_2SiF_6 Cs_2SiF_6 Tl_2SiF_6	2.21 2.17 2.19 2.21	2.20	2.26 ± 0.20
ClO_4^-	$KClO_4$ $RbClO_4$ $CsClO_4$ $AgClO_4$ $TlClO_4$	2.42, 2.36, 2.34 2.37, 2.36	2.37	2.43 ± 0.18
SO_4^{-2}	Na_2SO_4 K_2SO_4 Cs_2SO_4 Rb_2SO_4	2.47, 2.36, 2.39 2.35	2.39	2.40 ± 0.20
CrO_4^{-2}	K_2CrO_4 Cs_2CrO_4 $CaCrO_4$	2.47 2.44 2.50	2.47	2.70

The crystallochemical radii of complex tetrahedral and octahedral ions, which we calculated from X-ray data, and the values of the radii of the same ions, calculated from A. F. Kapustinskii's equation from the heats of formation of the complex salts, are presented in the table.

The error with which the values of the radius were determined is presented in the table where the radius was found by the method of differences for several pairs of salts, containing the same complex ion. If the error is not shown, then the radius of the ion was calculated from only one pair of salts due to the lack of thermochemical data. References are given for values calculated by other authors.

A consideration of the data in the table shows that the radii of the complex ions, calculated from thermochemical data, are in good agreement with the corresponding crystallochemical radii of the same ions, found from x-ray analysis data. The scatter of the radius values is most probably caused by the fact that the calculation involved four thermochemical values and each of these was determined experimentally with a certain error.

The truth of this hypothesis is confirmed by the fact that when the ionic radii were calculated from the less accurate values of the heats of formation of the complex salts, presented in summary [10], a corresponding greater scatter in the values of the ionic radii was obtained.

The salts considered in this work, containing complex ions, $MX_6^{\pm n}$, refer to compounds with a crystal structure of the type $K_2[PtCl_6]$.

We consider it our pleasant duty to thank K. P. Mishchenko for valuable critical observations.

SUMMARY

1. The crystallochemical radii of 18 complex ions of octahedral and tetrahedral configurations were calculated from x-ray structural data.

2. By means of A. F. Kapustinskii's equation, the radii of 14 complex ions of the same type were calculated from thermochemical data.

3. In the case of salts containing the ions CrO_4^{-2}, SO_4^{-2}, and ClO_4^-, and in the case of salts containing the complex ions MX_6^{+2} and having a crystal lattice of the $K_2[PtCl_6]$ type, good agreement was observed between the values of the crystallochemical radii of the complex ions and the values of the radii of the same ions, calculated by the method indicated in point 2.

4. It was shown that A. F. Kapustinskii's equation gives good results in calculating the crystal lattice energies of salts formed by complex ions of octahedral and tetrahedral configurations.

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** In Russian.

*** As in original - Publisher's note.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.